

CFTRI-MYSORE



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1. ~~resinous~~ state
 2. ~~polymerization~~.
 3. ~~polymeric~~ materials.
 4. ~~polymers~~.
 5. ~~synthetic~~ plastics
 6. ~~rubber~~ 7. ~~cellulose~~.
 8. ~~industrial~~ resins
 9. ~~fabrication~~.

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THE TECHNOLOGY OF PLASTICS AND RESINS

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PREFACE

This book is based upon a college course in the Chemistry of Plastics and Resins offered at Boston University by one of the authors. At the time that the course was originally planned, a survey of the books available on plastics and resins revealed that they were written either for graduate students of chemistry or for persons who wanted to know about the practical applications of plastics and resins without paying much attention to the chemical reactions involved in their preparation. Since the preparation of new plastics has been accompanied by improvements in processing techniques, it is desirable for the student to become familiar with both of the fundamental phases and try to correlate them as much as possible. Our objective, therefore, has been to develop a book which would be suitable for students who have had introductory courses in General Chemistry and Organic Chemistry, and which would serve as an adequate introduction to both the chemistry and the practical utilization of plastics and resins. The material should also be of interest to men in industry who wish to refresh their knowledge of the fundamentals underlying plastics development and technique.

The book is divided into three sections. The first section, consisting of six chapters, is the theoretical and general part, in which terms are explained, types and mechanisms of polymerization are discussed, and the relationship between various physical properties and the structure of plastics and resins is presented.

In the second section (thirteen chapters), the methods of preparation and the properties and uses of the more important resins and plastics are discussed.

The third section (six chapters) contains a discussion of fabrication techniques, e.g., compounding and mold designs, together with molding, casting, laminating and coating procedures.

The authors are especially indebted to Dr. Ernst A. Hauser of the Massachusetts Institute of Technology who read the original manuscript and made numerous suggestions for its improvement. We are also grateful to the several specialists who have read certain sections of the manuscript. While most of the suggestions made by these reviewers have been accepted and incorporated in the book, the authors hasten to add that they alone accept full responsibility for all statements made in this book. Criticisms and suggestions for improvement will be welcomed.

We are indebted to numerous chemical companies which have supplied glossy prints for the pictures in the book. Proper acknowledgments have been made below each picture.

The authors wish to express their appreciation of the suggestions and encouragement provided by Dr. J. Teppema of the B. B. Chemical Co. Our thanks are also due to Miss Marguerite F. Syner, Miss Helen Tiews and Mrs. Joseph F. Manning for their aid in assembling the manuscript.

J.P.M.
J.F.M.

BOSTON, MASSACHUSETTS
November, 1944

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CHAPTER I

THE RESINOUS STATE

One of the large divisions of matter is that of amorphous solids. Such important and diversified natural products as rubber, cellulose, proteins, bitumens, pitches and asphalts, together with the numerous synthetic plastics which have been developed in recent years, illustrate the wide range of possibilities to be found in this class. Although an almost unlimited variety of physical and chemical properties can be found in the class of amorphous materials, there are certain fundamental properties which are common to all. In order to understand the essential characteristics of amorphous structures, it is necessary to review briefly the behavior of molecules in the three well-known states of matter: gaseous, liquid and solid.

The Gaseous State.—It is well known that a gas will occupy all of a given confined volume. It does not fill the volume completely in the sense that nothing else could be put into the space, but some of the gas will be found in every part of the enclosed space. Another characteristic of gases is that they are completely miscible with each other. The uniform mixture of the gases of the atmosphere illustrates this fact. A gas can be condensed to a liquid by cooling it to a sufficiently low temperature, either with or without the application of high pressures. This condensation is accompanied by an extremely large contraction of volume.

The kinetic-molecular theory of gases pictures the gaseous state as composed of small particles called molecules which are relatively far apart and are in a state of constant, rapid, random motion; really a buzzing atmosphere of jitterbug activity. This motion explains the observation that a gas occupies all of the volume in which it is enclosed. The relatively large distance between the molecules explains the possibility of molecules of other gases being mixed with the first gas in any given container. The condensation of the gas to a liquid is due to a tremendous decrease in the space between the molecules as a result of low temperature and/or the application of pressure. Another result of this motion of the gas molecules is that collisions occur between molecules and also between molecules and the walls of the container. These latter collisions are the cause of the pressure exerted by the gas. Incidentally, these collisions are

perfectly elastic, i.e., the molecules do not lose any of their kinetic energy as a result of the collisions.

The decrease in the volume of a confined gas with an increase in the pressure to which it has been subjected (temperature constant), and the increase in the volume with an increase in the temperature (pressure constant), have been combined in a single mathematical expression, $PV/T = k$. This equation can also be expressed as $PV = nRT$,

where P = pressure

V = volume

n = number of moles of gas

R = molar gas constant

T = absolute temperature.

Although this equation represents the behavior of an ideal gas, it has been found that the equation is not accurate when measurements are made at high pressures or low temperatures. These variations are represented graphically in Figures 1.1 and 1.2. In Figure 1.1 it is obvious that PV is not at all constant as the pressure is increased. Figure 1.2 represents the deviations from the ideal gas law with variations of both temperature and pressure. One source of error is due to the fact that, although the space between the molecules of a gas can be compressed, the molecules themselves are practically incompressible. A correction may be made for the volume occupied by the molecules, and the volume factor in the above equation becomes $V - b$. When high pressures or low temperatures are used, it is found that the contraction in volume is greater than it was expected to be. This is attributed to the mutual attraction existing between molecules as they approach each other. This attraction is represented by the term a/V^2 and the final gas equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = nRT.$$

The Liquid State.—When a gas is subjected to a high pressure, the space between the molecules is decreased enormously, the attractive forces of the molecules increase and the gas changes to a liquid. The same effect can be produced by cooling the gas to a low temperature. In most cases of liquefaction of gases, both high pressures and low temperatures are utilized. The general characteristics by which a liquid is differentiated from a gas are:

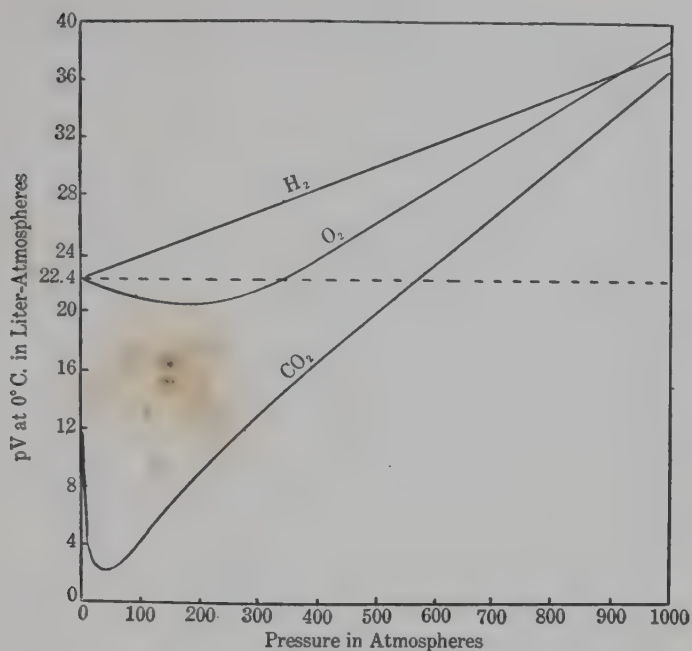


FIG. 1.1. Variation of PV with change of pressure. (Getman and Daniels, *Outlines of Physical Chemistry*, Seventh Edition, p. 21, J. Wiley and Sons, Inc.)

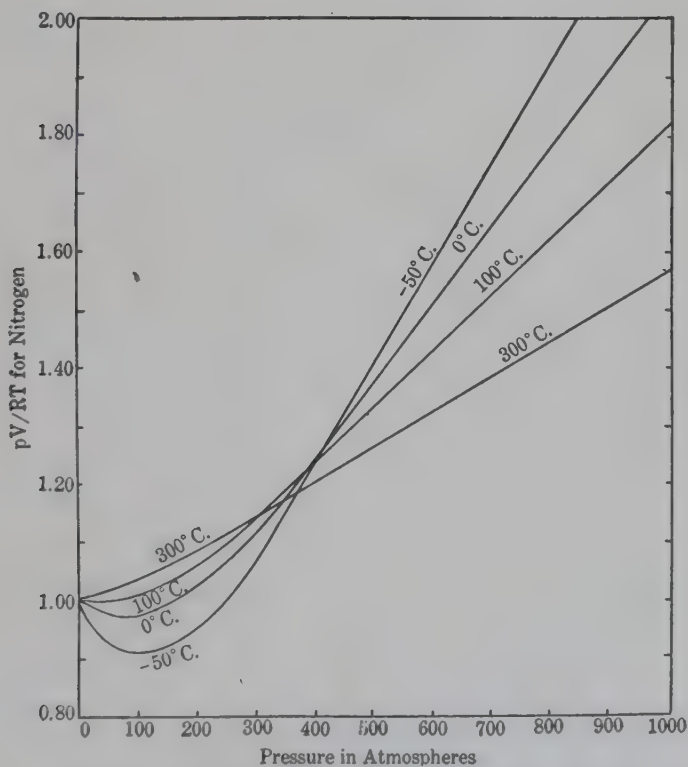


FIG. 1.2. Deviations from ideal gas law shown at various temperatures and pressures. (Getman and Daniels, *Outlines of Physical Chemistry*, Seventh Edition, p. 21, Wiley and Sons, Inc.)

1. Liquids offer a greater resistance to flow.
2. Liquids do not necessarily occupy all of a confined volume.
3. Liquids exhibit decreased compressibility.
4. Liquids have greater densities.
5. Many pairs of liquids are immiscible or only partially miscible.

All of these common properties of liquids can be predicted on the basis of the kinetic-molecular theory. Due to the large internal attractive forces between the molecules, their motion is limited, and the liquid does not completely fill a given container. These same forces cause a greater resistance to flow on the part of a liquid. Since the space between the molecules has already been decreased enormously in changing from a gas to a liquid, it follows that there is but very little opportunity for further compression. The fact that a large volume of gas is changed to a small volume of liquid means that there is a much greater weight of liquid occupying a given volume than of gas occupying the same volume. Hence, the density of a liquid is greater than that of a gas.

The magnitude of the cohesive pressure resulting from the internal attractive forces of the molecules of a liquid can be shown by a consideration of the extremely high degree of volume reduction which occurs on transition from the gaseous state to the liquid state. For example, 31,000 cc. of steam at 100° C. and one atmosphere of pressure will condense to a volume of 18 cc. of water at 100° C. and one atmosphere of pressure. The ratio, 31,000:18, represents the number of atmospheres of external pressure that would be necessary to compress this 31 liters of gas to liquid if the gas behaved as an ideal gas and if no intermolecular forces were involved. The pressure in this case is approximately 1700 atmospheres. This is the internal force which holds the molecules in this compressed form, and is known as the "internal pressure" of the liquid. The internal pressures of a few other liquids are:

Ether	3,100 atm.
Carbon Tetrachloride	3,640 atm.
Benzene	4,050 atm.
Bromine	6,000 atm.
Mercury	13,050 atm.

The internal pressure of a liquid is opposed by the tendency of molecules at the surface of the liquid to change to the gaseous state. This is due to the fact that the molecules of a liquid are in constant motion and some of them, as they reach the surface of the liquid,

acquire a sufficient amount of energy to escape from the liquid into the space above the liquid. If the space above the liquid is enclosed, a condition of equilibrium is eventually established between the molecules of liquid changing to vapor and the molecules of vapor changing to liquid. The pressure exerted by this vapor is known as the vapor pressure of the liquid. As the temperature of the liquid is increased, the molecules move more rapidly, more and more molecules escape, and the vapor pressure increases. If the space above the liquid is not enclosed, the gaseous molecules escape into the atmosphere, and the phenomenon of evaporation occurs.

One of the most important characteristics of a liquid is its ability to act as a solvent. It is well known that some liquids, e.g., water and ethyl alcohol, will dissolve in each other in all proportions. Other liquids, e.g., water and benzene, are almost completely insoluble in each other. Water is a good solvent for many salts, but is not a solvent for fats. Benzene is not a solvent for salts, but is a good solvent for fats. It is interesting to recall that all gases are miscible, regardless of their chemical composition. This is due to the small attractive forces existing among the molecules of a gas. The question of miscibility of liquids and solubility of solids in liquids is one which depends upon the great attractive forces existing among the molecules. The nature and magnitude of these forces depend in part upon the chemical composition of the component parts of the mixture. Since solvents play a very important role in the practical utilization of plastics, it is worthwhile to consider a few facts concerning the mechanism of solvent action.

Compounds such as alcohols, acids, aldehydes, ketones, and esters are classed as polar compounds. In a polar molecule, the center of gravity of the positively charged particles of the molecule is different from that of the negatively charged particles. The farther apart these centers of gravity are, the more polar the molecule. The magnitude of the polarity of the molecule is termed the dipole moment which is defined as the product of either of the charges and the distance between the two centers of gravity. Since each polar molecule has a positive center and a negative center, the oppositely charged parts of two molecules may attract each other and cause association of the two molecules. This phenomenon of association of like molecules occurs frequently in the case of polar molecules.

Examples of non-polar compounds are the normal saturated hydrocarbons, symmetrical unsaturated hydrocarbons such as ethylene and acetylene, and benzene. Since these molecules have zero dipole moments, there is a minimum of attraction between them and

they have no tendency to associate. Other hydrocarbons, such as 1-butene and toluene, have small but measurable dipole moments. These values, 0.45×10^{-18} and 0.37×10^{-18} e.s.u. for toluene and 1-butene respectively, are small compared with those obtained for other organic compounds, (see Table I-1, p. 7). Although it is not strictly accurate, organic chemists frequently refer to the hydrocarbon part of a molecule as the non-polar part of the molecule and to the functional group, such as hydroxyl, carbonyl, and nitro, as the polar part of the molecule.

Except for the hydrocarbons, practically all organic molecules consist of a hydrocarbon or non-polar part and an "active" or polar part. Liquid compounds which have similar compositions have been found to be completely miscible. Similarly, in the case of solid solutes, the more closely the structure of the solid resembles that of the liquid, the greater will be its solubility. These observations have been summarized in the most fundamental rule governing solubility, namely, that the more closely the chemical structures of the solute and the solvent resemble each other, the greater the solubility. This rule can be expressed simply by the statement that "like dissolves like". Water and ethyl alcohol are both polar liquids which contain the polar hydroxyl group in common as a major portion of their structure and, consequently, are miscible in all proportions. In the higher molecular weight alcohols, the effect of the polar hydroxyl group becomes weaker as a result of the increasing proportion of the hydrocarbon, i.e., non-polar, part of the molecule. This is accompanied by a marked decrease in the solubility of the alcohol in water. Water and benzene do not mix because there is no attraction between the polar molecules of water and the non-polar molecules of benzene.

However, it would be incorrect to conclude that there is a simple, direct relationship between dipole moments and solubility. The dipole moments of the first ten members of the homologous series of normal alcohols vary from 1.6 to 1.7, the average being 1.67. The solubilities of these alcohols in water vary from complete miscibility for the first three members to less than 0.1% for the last three members. The dipole moments of some organic compounds are given in Table I-1. For comparison, the dipole moment of water is 1.84×10^{-18} .

Although a molecule of vegetable oil contains a polar ester group, its effect is overshadowed by the relatively large non-polar hydrocarbon parts of the molecule. Hence, such an oil is soluble in the non-polar solvent, benzene, but is insoluble in water. An interesting

TABLE I-1. DIPOLE MOMENTS OF ORGANIC COMPOUNDS ^a

Compound	Moment
<i>n</i> -Hydrocarbons	0.0
Benzene	0.0
<i>n</i> -Acids	0.8×10^{-18}
Formic Acid	1.2
Ethers	1.2
<i>n</i> -Alcohols	1.67
Phenol	1.7
Esters	1.8
Alkyl Chlorides	2.0
Ketones	2.7
Nitrates	2.9
Nitroparaffins	3.1

^a Gilman, *Organic Chemistry, An Advanced Treatise*, Vol. II, 2nd ed., p. 1754, John Wiley & Sons, Inc., New York, 1943.

comparison based on the above generalizations has to do with the insolubility of linseed oil in ethyl alcohol and the solubility of castor oil in ethyl alcohol. Molecules of both these oils have comparable hydrocarbon parts and the same ester groups. The castor oil molecules, however, have three hydroxyl groups which the linseed oil molecules do not have. These hydroxyl groups of the castor oil molecules attract the hydroxyl groups of ethyl alcohol with the result that castor oil is readily soluble in ethyl alcohol. Since linseed oil does not have any hydroxyl groups, alcohol molecules are not attracted and miscibility does not occur.

The Solid State.—The change from the liquid state to the solid state occurs at the freezing point of the substance concerned. Whereas a gas may be changed into a liquid by suitable adjustment of pressure or temperature, the principal factor involved in changing a liquid to a solid is a decrease in the temperature. Pressure plays only a very minor part in this kind of change, as would be expected from the fact that the volume occupied by the solid is practically the same as that of the liquid from which it is formed. Consequently, the densities of a substance in the solid or liquid states are practically identical. An important exception to these general statements is that water expands as it freezes, so that the density of ice at 0° C. is appreciably less than that of water at 0° C. The reduction of the temperature, when changing a liquid to a solid, is accompanied by a decrease in the kinetic energy of the molecules involved.

The typical characteristics of the solid state are:

1. Solids have a definite shape and occupy a definite volume.
2. Solids exhibit the qualities of hardness and compactness.
3. Most solids melt at a definite temperature or within a definite temperature range.
4. Most solids have only a slight tendency to sublime.

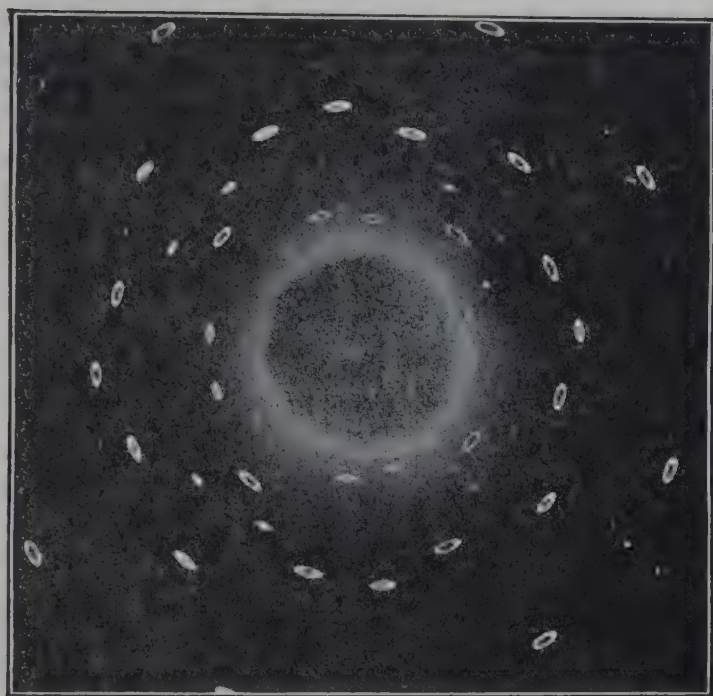
The attractive forces between molecules and the polar characteristics of certain molecules are fully as important in the case of solids as in the case of liquids. The attraction between the molecules of a solid is so great that the movement of molecules is limited to rotation or vibration about a fixed, mean position. The extent of this motion is dependent upon the chemical composition and the temperature of the substance concerned.

The specificity of the forces involved in the formation of solids is illustrated by the fact that crystals of one compound rarely occlude crystals of another compound. In fact, the forces which are involved in the formation of crystals act in such a way as to exclude any matter that is foreign to the crystal structure being formed. This idea is similar to that proposed by Ostwald¹ for the coagulation of colloidal particles by the addition of electrolytes. Ostwald proposed that the colloidal particles or micelles form part of a highly dispersed ionic lattice in the solution. When electrolytes are added to such a solution, the interionic forces become so great that the micelles are pushed together and are expelled from the ionic lattice. This property of excluding foreign matter from a growing crystal lattice is utilized in purifying solids by a process of recrystallization from a suitable solvent.

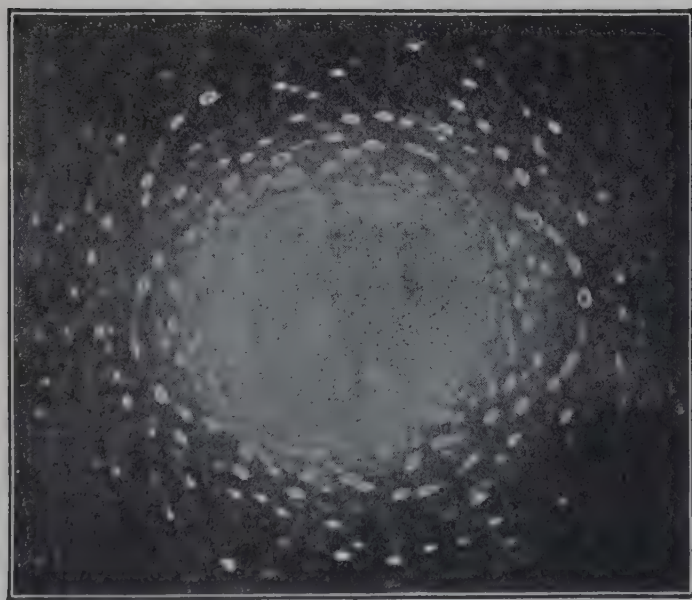
The attractive forces which exist in solids give rise to two distinct types of solids, (a) crystalline solids and (b) amorphous solids. In the crystalline state there is a definite arrangement or pattern of molecular or ionic parts, resulting from the well-ordered, directive action of the binding forces. In the amorphous state, there is no regular pattern of the molecular parts, because of the lack of a strong directive force. It is possible for a solid to exist in a state which is intermediate between the crystalline and amorphous states, namely, in a mesomorphic state.² The particles of such a solid are oriented only in certain directions and not oriented in other directions. Soap is an example of a substance which exists in a mesomorphic state.

¹ Ostwald, *J. Phys. Chem.* **42**, 981 (1938).

² Hauser, *Colloidal Phenomena*, p. 203, McGraw-Hill Book Co., New York, 1939.



(a) Laue diagram of magnesium oxide



(b) Laue diagram of potash alum

FIG. 1.3. Typical crystalline powder x-ray diagrams. (Taylor, *Treatise on Physical Chemistry*, Second Edition, p. 235, D. Van Nostrand Co., New York.)

The Crystalline State.—The most common and best-known type of solid matter is the crystalline solid. The regular periodic arrangement of constituent parts produces a definite type of x-ray diffraction pattern, plane surfaces on cleavage, a sharp melting point, and predominantly elastic properties when subjected to stress. Measurements of bond strengths, kinetic energies and crystalline structure may be obtained from a study of these fundamental properties. Such measurements have shown the existence of three distinct types of crystalline bodies, (1) primary valence crystals, (2) heteropolar crystals, (3) secondary valence crystals. The main difference among these classes is the nature of the force which holds the parts of the crystal lattice in a definite form.

Typical x-ray diagrams of crystalline solids are shown in Figure 1.3. The symmetrically arranged bright spots around the center halo are indicative of a crystalline structure.

Primary Valence Crystals.—This type includes those materials which are made up of atoms combined into a structural whole by primary valence forces. The



FIG. 1.4. Diagram representing structure of diamond crystal. (Bragg and Bragg, *X-rays and Crystal Structure*, p. 100, Harcourt, Brace and Co., New York.)

forces are of the same magnitude, directed at the same angles, and effective over the same distance that primary valence forces of the atoms concerned would ordinarily exhibit. The simplest illustration is the diamond, the structure of which is represented in Figure 1.4.

The crystal in this case consists of many carbon atoms, each linked to four neighboring carbon atoms placed at the corners of a tetrahedron. The usual inter-carbon distance and bond strength are existent.

Such crystals would be expected to possess unusually high hardness and melting point.

Heteropolar Crystals.—The second type, of which sodium chloride is the most familiar example, results from the transference of electrical charges between atoms.

In Figure 1.5, each solid circle (●) represents a sodium ion and each open circle (○) represents a chlorine ion. Examination of the

diagram shows that each sodium ion is surrounded by six chlorine ions and each chlorine ion is surrounded by six sodium ions. Due to the fact that these particles of sodium and chlorine are actually positive and negative ions, a high order of electrical attraction exists

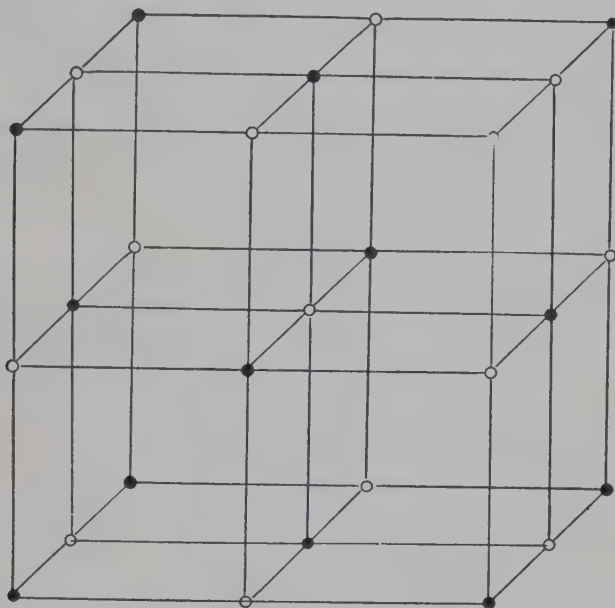


FIG. 1.5. Cubic arrangement of sodium chloride.

within the crystal, and a high melting point would be predicted. This type of crystal is characteristic of solids which are composed of positive and negative ions. However, it should not be inferred that all such crystals have a cubic arrangement, for several other crystal structures are possible.

Secondary Valence Crystals.—The majority of solid materials found in organic chemistry may be included in this class. The crystal owes its formation in this case to forces which most closely resemble the attractive forces described in the discussion of the internal pressures of liquids. They are forces left over from the exertion of the primary bonding by chemical reaction. These residual forces are referred to as *secondary valence* forces. When the effect of such a force is properly directive in its action it is capable of producing a well-ordered definite unit arrangement. Such common organic solids as naphthalene, nitrophenol, acetanilide and anthracene, are representatives of this class. The magnitude of the forces present in such a crystalline body is much less than that of the previous types. This results in a greater distance between the constituent molecules and consequently decreased density.

The magnitude of the forces actually existent may vary widely from one compound to another. Proof of this variation may be obtained from such a physical measurement as the melting point. Materials of low intermolecular attraction melt at a lower temperature than those of high intermolecular attraction. Naturally, the class as a whole is made up of materials which melt at much lower temperatures than substances bound into a crystal lattice by either primary valence or heteropolar forces.

The three types of crystals may be compared on the basis of the magnitude of force exerted and the distances over which the force acts:

TABLE II-1 ^a

Crystal Type	Energy Content of Bond	Distance Between Constituent Parts
Primary valence	100 kcal.	1-1.5 Å ^b
Heteropolar	100 kcal.	2-3 Å
Secondary valence	1-10 kcal.	3-4 Å

^a Data taken from Lewis, Squires and Broughton, *Industrial Chemistry of Amorphous Materials*, p.274. The Macmillan Company, New York, 1942.

^b One Ångstrom unit (Å) is equivalent to one ten-millionth of a millimeter (10^{-7} mm.).

The Amorphous State.—The amorphous state has previously been described as distinct from the crystalline state in that there is no regular arrangement of the component molecules. The heterogeneous arrangement which is characteristic of the amorphous state is due to the lack of strong directive forces among the molecules involved. Since liquids are believed to have a random arrangement of the molecules, amorphous solids have frequently been described as supercooled liquids. Glass, asphalt, pitch, rubber, and numerous resins, both natural and synthetic, are examples of amorphous solids which have considerable industrial importance. Mention has already been made (p. 8) of the mesomorphic state as intermediate between the crystalline and amorphous states. Some very important substances exist partly in the crystalline state and partly in the amorphous. For example, cellulose appears to consist of crystalline portions interposed with amorphous material. Rubber, at room temperature, exists in the amorphous state, but if rubber is either stretched or cooled, it exhibits a certain amount of crystallinity.

Although there are great differences in the properties of various amorphous substances, there are a few general characteristics of the amorphous state. These characteristics are:

1. Amorphous solids do not have a definite melting point.
2. There is no regular, ordered arrangement of the molecules in the solid.
3. When the solid is broken, a conchoidal fracture results.
4. When subjected to stress, the solid exhibits a tendency to flow.
5. The measurement of physical properties is not dependent upon the direction in which the measurement is made.

The resinous state may be characterized by these properties. Substances which belong in the mesomorphic state exhibit some of the characteristics of amorphous solids and are frequently considered as belonging in the resinous state.

The important resins may be subdivided into the following categories: *natural*, *synthetic*, *artificial*. The first two types refer to the source of the material being investigated. *Natural*, of course, refers to the existence of the substance in one form or another in nature. *Synthetic resin* is the class name for the products of amorphous character which are produced by a reaction between non-resinous bodies. The term, *artificial resin*, explains more than the source of the resin. Actually, an artificial material is one which owes its importance to a duplication of the properties of some other material of natural origin. Although synthetic means might be utilized in the production of such a material, the lack of unique, distinct properties makes it an artificial type.

The intermolecular attractive forces which were emphasized in considerations of both the liquid and solid states also explain many characteristic phenomena of the amorphous bodies. In the first place, the physical structure of these amorphous types differs from solids of a crystalline nature principally in the degree of molecular regularity exhibited. A high magnitude of attractive force with no directive forces operating results in a haphazard arrangement. Equally strong forces in the crystalline body, however, produce a well-defined lattice arrangement because of the predominating effect of directional lines of force.

The maximum effect of attraction in the case of amorphous materials is produced when the random, jumbled pattern of molecules is "combed out" into some degree of crystallinity or regular arrangement. Rubber, for example, ordinarily exhibits the characteristic x-ray diffraction pattern of amorphous substances. The broad halo

evident under these conditions is replaced, however, by a spot diffraction pattern when the rubber is stretched. By this external physical operation the molecules become aligned and the attractive forces exert their maximum effect. The x-ray diagrams of unstretched and stretched rubber are shown in Figures 1.6 and 1.7.

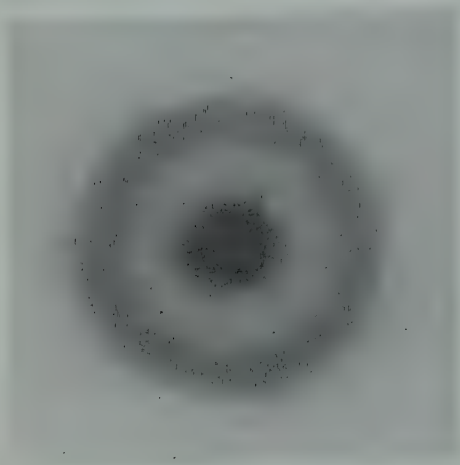


FIG. 1.6. X-ray diagram of unstretched rubber, showing simple amorphous band. (Courtesy of Ernst A. Hauser, Massachusetts Institute of Technology.)



FIG. 1.7. X-ray diagram of rubber stretched 600%, showing spot diffraction pattern. (Courtesy of Ernst A. Hauser, Massachusetts Institute of Technology.)

Other properties characteristic of the resinous state are explained on the basis of molecular structure. The theoretical interpretation of many are reserved for a later chapter. The place of resins in the chemical world is regulated by the attributes of the amorphous class of materials. Correlation of the properties actually displayed with those which might be predicted from theoretical considerations has important industrial significance. To provide the necessary background for such a correlation has been the purpose of this chapter, namely a comparison of the gaseous, liquid, crystalline, and resinous states of matter. Proteins, cellulose, rubber, natural gums and resins are the basic substances with which the newer synthetic resins may be compared and related.

Review Questions

1. What is the relationship of the molecules and their attractive forces to one another in each of the states: gaseous, liquid, and solid?
2. Explain the meaning of polarity in an organic molecule. What is its effect on solubility?
3. How does the arrangement of molecules in copper sulfate and rosin (a natural resin) differ? To what group does each belong?
4. What is meant by each of the following terms:

primary valence
secondary valence
amorphous
crystalline
resinous?

CHAPTER II

THE PLASTIC STATE

The industrial importance of amorphous materials lies in their behavior under conditions of stress. Most substances of this class are generally useful in a variety of applications because of the possibilities of varying the strain which results from a fixed stress. The ease of deformation of these amorphous materials may be altered in various ways, depending on the material being used. Heat, water, organic solvents, or mechanical shear may all act, under certain conditions, as agents for the deformation of resinous bodies. Thus, resins, both natural and synthetic, become plastics at some time during the course of their manufacture or application. By definition, a *plastic* is recognized as a material which is susceptible to deformation and is capable of retaining the new form. Accordingly, *plasticization* refers to the art of making a material plastic. It is in this form that synthetic resins exhibit their outstanding properties and adaptability to numerous industrial applications. While in a plasticized state, industrial operations such as molding, extrusion, laminating, casting, and bonding are carried out.

Methods of Plasticization.—The term, *plastic*, implies many conceptions not included in the definition. The degree of plasticity is almost invariably dependent upon such factors as temperature, rate of stress, and previous treatment. A material such as glass, for example, may be readily deformable when heat is applied and be capable of retaining the deformation permanently when deplasticized by cooling. The art of glass-blowing is founded upon such behavior. The rate at which deformation is attempted is an important characteristic. Many substances which are ordinarily fragmented by sudden impact may be deformed slightly, without being heated, under the effect of a gradual stress. The previous treatment, likewise, alters the plastic range of various materials. An extreme case is found in the phenol-formaldehyde resins which become heat-resistant and insoluble during the process of molding at an elevated temperature. By such treatment the plastic capabilities of the base material are completely altered. Whether or not such a molded article should be classed as a plastic is a much-debated question.

Some chemists claim that its inability to be deformed by any of the usual methods prevents its inclusion. Others argue that its formation from a plastic material by heat plasticization followed by chemical hardening or deplasticization is sufficient to place the molded form in the field of plastic materials.

The variability of plasticization methods—heat, pressure, water, solvents, non-solvents—permits many materials which otherwise would never reach a plastic state to be included. The prevalence of materials and applications in which the principles of plasticization are applied is astounding. So too, are the widespread possibilities of changing the degree or period of plasticization to fit particular products. Common materials such as clay, leather, rubber, wood, and paper are essentially products of nature which are applied in almost limitless ways. The property common to all is their ability to be formed or shaped under some condition of plasticization. Upon removal of the plasticizing means, the imparted shape is retained.

In some cases, the plasticity originally imparted to the raw compound is allowed to remain even after application. A different type of plastic behavior is involved, therefore, in such a material as plastic wood as compared with a permanently soft caulking or seam-sealing compound. In the former case the practical use of the material necessitates a deplasticization step; in the latter illustration, however, a reduction of plasticity after application is not desirable.

In the field of synthetics, plasticization in all forms is probably of even greater importance than in the case of natural products. The entire art of the manufacture of a synthetic product is built about a particular type of plasticization. In the inorganic field, for example, such materials as glass, steel, and concrete may be cited as typical plastics. Organic materials which undergo plasticization and, usually, deplasticization in their application include most of the synthetic resin types, such as phenol-formaldehyde and urea-formaldehyde resins, cellulose acetate, nylon, polystyrene, and polyvinyl copolymers.

Plasticizers.—Any ingredient which remains in the finished, solid product and which is used to increase the ease of plasticization may be classified as a *plasticizer*. To be effective as such, the material must have a low evaporation rate to prevent loss from the fabricated article and it should possess some solvent power for the material being plasticized. If a completely non-solvent type of plasticizer is used, there is danger that aging will cause embrittlement of the fabricated plastic. This will occur because of *bleeding-out* of the

non-solvent on the surface after slow diffusion from the interior. In any case, the amount and type of plasticizer which might be used in any application will depend upon the solvency, susceptibility of the base material to plasticization methods, the application technique being used, and the degree of rigidity desired after fabrication. The composition, consistency, and form of the chemical plasticizers may also vary widely. Possibilities range from simple organic liquids to soft, gum-like or low-melting resins.

Although the form and degree of plasticization and deplasticization may vary widely, the procedure for the application of plasticization methods follows a more or less stereotyped pattern. After the preparation and purification of the base material, natural or synthetic resinous product, plasticization is effected by one of the common methods. In the plasticized form deformation is carried out and is then followed by complete or partial deplasticization to set the product in the desired shape. Since the degree of set varies according to the fabrication, the most suitable means of producing the desired plastic state must be determined in each case.

Types of Plasticity.—Several different types of plasticity have been hinted at in the preceding discussion. Two, in particular, are worthy of further comment. In the first instance, no liquid is present to act as a plasticizing medium. The effect depends entirely upon the thermal properties of the material. An example of this type is the deformation of a pure phenol-formaldehyde resin by the use of heat and pressure. An increase in the temperature causes an increase in the kinetic energy of the molecules so that they move more freely with respect to each other. When pressure is applied simultaneously, deformation of the plastic material results. In such a case the temperature is the deciding factor in the regulation of the plasticity. A type of plasticity which can occur in crystalline bodies, particularly metals, even in the absence of a liquid phase is also known. The main difference between the plasticity described in the case of phenol-formaldehyde resins and that peculiar to crystalline bodies is the fact that temperature has no particular effect in the latter case. Instead of increased motion of molecules being involved, the plastic change under the influence of pressure is due to a gradual slippage of one molecule over another. An exchange of molecular positions relative to one another results in a deformation. Because temperature is unimportant, the material possesses athermal plasticity. Although such a phenomenon exists in certain types of crystalline matter, the application of plasticization methods to crystalline bodies is rare.

The plasticity caused by heat in the case of phenol-formaldehyde resins may be aided by the simultaneous use of a liquid plasticizer. When added to a resin base in the compounding of a molding powder, a liquid plasticizer increases the ease of plasticization because it increases the effect of temperature. The molding composition softens and flows in the mold at a lower temperature than the resin alone would. This, then, is an example which illustrates the use of two plasticization methods—heat and solvents. The material being molded has changed from the completely solid-type plastic described above, to a liquid-solid plastic, because both phases are involved.

The latter plasticity type is better illustrated by cases in which a liquid chemical plasticizing agent is the only plasticizing effect used. Simple organic compounds are used in the formulation and application of plastics in such fields as coatings, lacquers, varnishes, **fibers**, and paper manufacture. Often the chemical plasticizer is allowed to remain in the plastic film. By use of the optimum amount, desirable properties are obtained, particularly in the case of the permanently heat-softened resins used for coatings, adhesives, and extruded fibers or tubes. Characteristics of resiliency and flexibility are imparted by incorporation of amounts ranging from 10–70% of a slow-evaporating liquid or, rarely, a low-melting solid. Plasticization by means of a solvent is also used as a fabrication method in cases in which it is desirable to permit the solvent to leave the film when spread. Thus, in the lacquer and varnish industries, low-boiling, simple organic solvents act as temporary plasticization agents for a resin base. Deplasticization then results from evaporation of the solvent.

Colloidal Characteristics of Liquid-Solid Type of Plasticity.—In such liquid-solid types of plasticity a degree of colloidal behavior is characteristic of the material. As in the case of colloids, also, certain fundamental concepts are of importance in determining the properties of the plastic body. These factors may be summarized as follows:

1. Specificity of plasticizer.
2. Extent of dispersion.
3. Magnitude of attractive intermolecular forces.

The specific effectiveness of the liquid used as the dispersing medium is important. The nature and the amount of the chemical plasticizer are both capable of altering the degree of plasticity. The liquid should, preferably, have some solvent power for the solid. As mentioned above, better plasticities are obtained with solvent plasticizers than with non-solvent plasticizers.

The extent of the dispersion of the solid particles in the liquid phase is also an important factor. In order to achieve satisfactory plasticity, the molecular aggregates must be broken down or dispersed until the particle size is between the optimum limits of $0.3\text{--}3\mu$. The more uniform the particle size the better the plasticity obtained. It should be emphasized that this discussion is concerned with a state which is close to the borderline of a solid possessing plastic flow and a liquid which exhibits viscous flow.

A plastic solid is one which will retain its shape unless acted upon by some outside force such as an increase in temperature or the application of pressure. This results from the fact that there are fairly strong attractive forces among the particles which cause resistance to flow. However, these internal attractive forces must

TABLE I-2. PLASTICIZATION MANIPULATION

Method	Plasticity Achieved by	Deplasticized by	Application
Heat	Softening	Cooling	Heat-softened resins, glass
	Softening	Chem. Reaction: Heat hardened	Thermosetting resins
Solvent	Complete solution	Evaporation	Adhesives, lacquers
	Complete solution	Coagulation in non-solvent	Cellophane, rayon
	Partial solution	Evaporation	Nitrocellulose
	Swelling	Evaporation and chemical reaction	Concrete, ceramics
Plasticizer	Dispersion in solvent of low evaporating rate	None	Molding, coatings
	Dispersion in non-solvent of low evaporating rate	None	Rarely used except in conjunction with solvent plasticizer

be capable of being overcome by the application of an external force in order to cause plastic flow. If the particles in this type of plastic solid are too small, they may exhibit the Brownian movement¹ to such an extent that the solid does not retain its shape under normal

¹ The Brownian movement is the term used to describe the movement of particles in a colloidal suspension which occurs as a result of the random, irregular bombardment by molecules of the solvent.

conditions and possesses the characteristics of a very viscous liquid. On the other hand, if the particles are too large, there will not be sufficient attraction among the particles for the existence of the solid state and the dispersion will be a liquid.

The strength and character of the attractive forces existent among the solid particles play a part in determining the degree of plasticity. Since the strength of these forces is dependent not only on the specific chemical nature of the materials used, but also on the thickness of the liquid interface separating the particles, the importance of concentration is obvious. In an extreme case, the attractive forces between the solid particles may be sufficiently high to result in a phenomenon known as *thixotropy*. When a material is so classified it has the peculiar ability of solidification when at rest and liquefaction when agitated.

The three most important methods of plasticization and procedures used are summarized in Table I-2.

Effect of External Forces.—On application of an external force to an amorphous solid, a deformation will be produced. The extent and permanency of the deformation will depend upon a number of factors such as the rate of stress, amount of force applied, and temperature. Before discussing the effects produced on an amorphous solid, it will be worth while to compare the effects of a distorting force on a crystalline solid and on a liquid. The solid state differs from the liquid state particularly in its inability to deform under any force less than a finite one, and its inability to transmit the external force throughout the entire mass. Thus, local stresses of a measurable range produce, in the case of crystalline solids, a deformation proportional to the distorting force. The dimensional change, particularly in low ranges of stress, results in a recoverable deformation or, in other words, an *elastic* change. Liquids, on the other hand, respond to stresses of very low magnitude by transmission of the strain from localized regions and by deformations of both an elastic and a non-elastic nature.

Deformation under stress in the case of amorphous materials involves a consideration of the principles applied to both liquids and crystalline solids. The immediate apparent effect of a small distorting effect applied to such substances is the production of an elastically recoverable deformation. It soon becomes apparent, however, that even the slightest load when applied over a long period of time will result in some changes which are not recoverable. Two effects, therefore, are caused by an external stress. The total deformation (D) is then the sum of an elastic change (E_d), and a

non-elastic change (P_d). The permanent distortion resulting after release of the distorting force is known as a *permanent set* and is, of course, equal to the non-recoverable distortion.

The effect of *creep* or plastic flow does not usually become evident until the distorting force has passed a definite minimum which is specific for each material investigated. This minimum force is known as the *elastic limit*. Below this figure a distorting force causes a change which is completely recoverable when the force is removed. In such cases, the experimentally determined values are in good agreement with Hooke's Law for Elastic Strain,

$$F = E \frac{\Delta L}{L}$$

where F = external load

E = modulus of elasticity (see p. 60)

L = length of specimen

ΔL = elongation.

When the distorting force exceeds the elastic limit, the elongation is no longer proportional to the force applied and Hooke's Law no longer applies. The change is not completely recoverable when the force is removed, even though the force has been applied for only a short time. Hence a permanent set develops. In many cases it has been found that, above the elastic limit, the elongation continues even with a constant distorting force, as a result of plastic flow. Rupture of the sample may occur either as a result of the continued elongation under a constant distorting force or by increasing the distorting force.

In Figure 2.1, OA represents the elastic deformation which occurs practically instantaneously; AB represents the plastic deformation

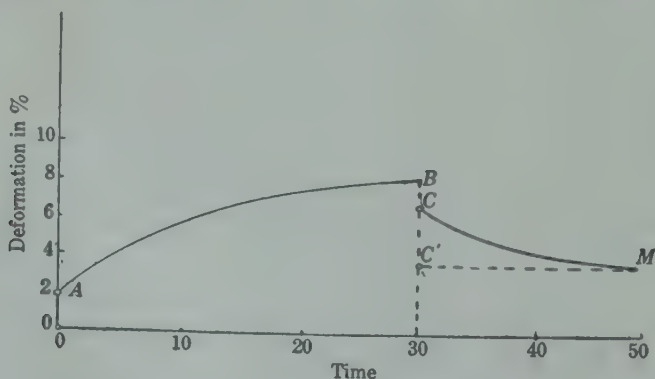


FIG. 2.1. Flow curve of typical high polymer.
(Mark, *Ind. Eng. Chem.* **34**, 453, 1942.)

occurring during a definite interval of time; BC represents the amount of deformation recoverable immediately after the force is removed; CM represents the amount of gradual recovery; and the percentage represented by the vertical distance between O and M represents the amount of permanent set developed.

The non-elastic deformation is similar to that which occurs in liquids. It is a flow characteristic which is another indication of the "supercooled liquid" nature of amorphous solids. As expected from its comparison to a liquid property, the degree of permanent set depends not only on the amount of stress applied but also on such experimental conditions as the rate of application and the temperature of testing. In the latter case, for example, the temperature will alter the flow characteristics. As the temperature is increased the elastic limit decreases, flow is increased, and permanent set values become larger. Likewise, addition of solvents or chemical plasticizers generally increase the plastic rather than the elastic characteristics when stress is applied.

Review Questions

1. What is the plastic state and what is the technique used for producing this condition?

2. Select typical plasticizers from the list:

ethyl alcohol
castor oil
benzene
dibutyl phthalate
glycerine
 α -amyl naphthalene.

3. What is deplasticization and why is it often necessary?

4. What are the three principal methods of plasticization? How may the degree of plasticization be regulated in each case?

5. What is meant by each of the following terms:

elastic limit
plastic flow
permanent set?

Summarize the effects of a distorting force on a plastic.

6. What effect does plasticization have upon the elastic limit?

7. If a slow, continuous stress and a rapid stress of equal magnitude are applied to similar samples and released, which would you expect to produce the greater permanent set?

CHAPTER III

POLYMERIZATION

The chemical world with which the study of plastic and resinous bodies is concerned is mainly one composed of large, bulky molecules which form amorphous solids. Although many of these amorphous materials occur in nature, e.g., rubber, cellulose, starch, proteins, and others are formed from numerous combinations of organic compounds, our knowledge of the chemistry of these substances has lagged considerably behind our knowledge of the chemistry of crystalline substances. This is due, in part, to the fact that until recently, the majority of organic chemists have preferred to work with crystalline compounds of a high degree of purity as shown by their sharp melting points. It is also due, in part, to the extreme difficulties involved in working with these amorphous materials. As a result of the research stimulated by an industrial interest in synthetic resins, both as substitutes for natural products and as new materials for specific purposes, our knowledge of these amorphous substances is increasing rapidly. The pioneer researches of chemists such as Emil Fischer, Staudinger and Carothers have shown that the fundamental atom-to-atom structure of these large molecules is the same as that found in the better-known smaller molecules. For example, the interatomic distances of C—C, C=C, C=O, and C—N, and the valence angles between atoms are the same in large molecules as in small molecules. Furthermore, many of the large molecules can be synthesized by using the same types of reactions that are used to synthesize smaller molecules.

Definition.—The type of organic reaction in which a complex molecule of high molecular weight is produced from many simple molecules is known as *polymerization*. The first definition of polymerization described it as a process in which two or more molecules of a single substance combine to form a single molecule which has the same empirical formula as the original molecule, but a higher molecular weight. The product of the reaction was called a *polymer*, a word which means literally "many parts." When paraformaldehyde was shown to have the formula $(\text{CH}_2\text{O})_n\text{H}_2\text{O}$ instead of $(\text{CH}_2\text{O})_n$, and when large polymeric type molecules were formed by condensation reactions involving the loss of water, ammonia or salt, this definition became inadequate. Carothers proposed that a polymer-

ization reaction be defined as consisting of "intermolecular combinations that are functionally capable of proceeding indefinitely."¹

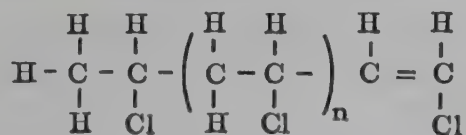
This definition includes both the self-addition and the condensation types of polymerization reactions.

Addition Polymerization.—The addition type of polymerization may be subdivided into three classes:

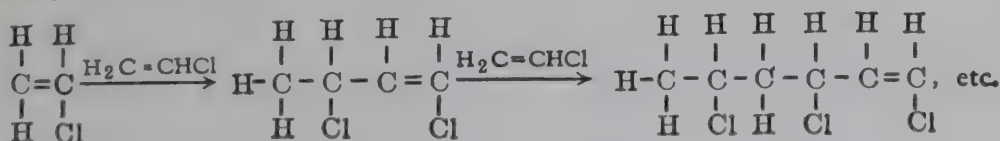
1. Simple polymerization.
2. Copolymerization.
3. Heteropolymerization.

Simple polymerization is a reaction which involves only a single species. This type of reaction can be represented by the polymerization of vinyl chloride, $\text{CH}_2=\text{CHCl}$ to form polyvinyl chloride, $\left(\begin{array}{cc} \text{H} & \text{H} \\ | & | \\ -\text{C} & - & \text{C}- \\ | & | \\ \text{H} & \text{Cl} \end{array} \right)_n$. The polymer has the same empirical formula as the start-

ing material, (often called a monomer), but the molecular weight is some integral multiple of the molecular weight of the monomer. The question arises immediately concerning the apparent free valences of the terminal carbon atoms of the polymer. While these valences may be satisfied by atoms or groups obtained from the solvent or the catalyst, the nature of the terminal groups is not yet known in most examples of addition polymerization. One of the early proposals to account for the terminal valences was to assume ring formation. This idea has been abandoned because of the overwhelming evidence for the existence of linear polymers. Still another assumption that has been made is that a double bond exists at one end of the molecule and a hydrogen atom satisfies the terminal valence at the other end of the molecule, e.g.



In this case a hydrogen atom is assumed to migrate from the second carbon at one end of the chain to the first carbon at the other end of the chain. An alternative explanation is that the polymer grows by the addition of one molecule of vinyl chloride to the polymer already formed, e.g.,



¹ Carothers, *Trans. Faraday Soc.* 32, 41 (1936).

Copolymerization occurs when two or more different molecular species, each capable of polymerizing alone, combine to form a large molecule (often called a macromolecule) which is composed of units of each monomer. For example, vinyl chloride can be polymerized to polyvinyl chloride and vinyl acetate can be polymerized to polyvinyl acetate. A mixture of vinyl chloride and vinyl acetate can be polymerized to form polymeric molecules which contain both vinyl chloride and vinyl acetate units. If A represents a vinyl acetate unit and C represents a vinyl chloride unit, the polymer may be represented as $-C-C-A-C-A-C-C-C-A-$ etc. While the percentage of each unit in the polymer molecule can be determined, the order in which the units enter the growing molecule is not yet known. The chemical and physical properties of copolymers are dependent not only upon the size of the macromolecules produced but also upon the relative proportions of the reacting monomers.

Heteropolymerization is similar to copolymerization. In this case, however, one of the monomers is a compound which does not polymerize by itself, even though it is structurally capable of undergoing polymerization. Maleic anhydride, $\begin{array}{c} \text{HC}-\text{C}=\text{O} \\ \parallel \quad \diagup \text{O} \\ \text{HC}-\text{C}=\text{O} \end{array}$, possesses a double bond similar to that found in vinyl chloride, but maleic anhydride does not combine with itself to form a polymer. Styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, which polymerizes easily to form polystyrene, will react with maleic anhydride to form a heteropolymer containing both styrene and maleic anhydride units, e.g. $\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2- \\ | \quad \quad \quad | \quad \quad \quad | \\ \text{C}_6\text{H}_5 \quad \quad \quad \text{O} \quad \text{O} \quad \text{C}_6\text{H}_5 \end{array}$ etc.

The effect of variations of chemical structure on the ease of polymerization will be discussed later (p. 28).

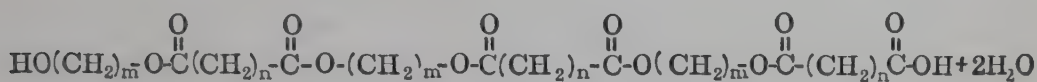
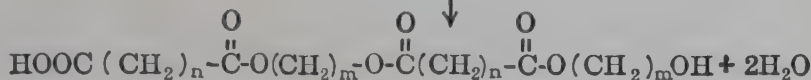
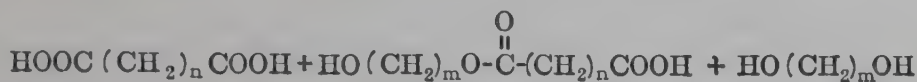
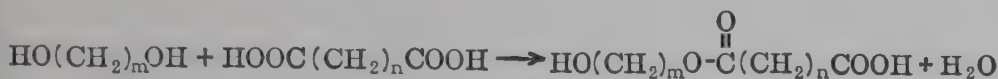
Condensation Polymerization.²—A condensation type of polymerization reaction is one which occurs with the elimination of some simple molecule such as water, ammonia, salt, hydrogen chloride, or hydrogen sulfide. One of the best-known reactions in organic chemistry is the reaction between an acid and an alcohol, forming an ester and water.



If a dicarboxylic acid and a dihydroxy alcohol are used, the reaction does not stop when one molecule of acid has reacted with one molecule of alcohol. The resulting molecule possesses both a hydroxyl group and a carboxyl group and hence is capable of reacting with another

² Carothers, *Chem. Rev.* **8**, 358 (1931).

molecule of acid and another molecule of alcohol. As will be seen from the reactions indicated below, this type of reaction is capable of continuing indefinitely.



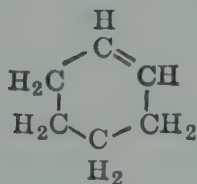
In this particular illustration, if an excess of the dihydroxy alcohol is used, the terminal groups will be hydroxyl groups, whereas an excess of dicarboxylic acid will yield a polymer whose terminal groups are carboxyl groups.

Instead of using a dihydroxy alcohol and a dicarboxylic acid, it is possible to use a diamine and a dicarboxylic acid to form a polyamide, as in the manufacture of Nylon. A dihalide will react with sodium polysulfide to form a polyalkyl polysulfide, such as Thiokol. Both of the functional groups may be present in the same molecule, e.g., a dihydroxy alcohol could be used to form a polyether or a hydroxy acid could be used to form a polyester. By varying the composition of the radicals to which the functional groups are attached, it is obvious that many variations in the properties of the resultant polymers can be obtained.

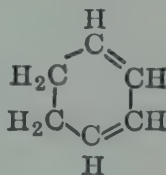
If each of two different reacting molecules has two functional groups, the reaction is called a bi-functional reaction. If one of the molecules has two functional groups and the other has three functional groups, the reaction is bi-trifunctional. A tri-trifunctional reaction occurs if both reacting molecules contain three functional groups. The number of functional groups involved plays a very important part in determining the composition and the properties of the polymer produced.

Effect of Chemical Structure in Addition Polymerization.—The one outstanding structural requirement for polymerization of the addition type is unsaturation. Although polymers have been obtained by subjecting saturated gaseous hydrocarbons to the action of alpha rays³ or high-voltage electrical discharges, it has been found that hydrogen and methane were also formed. This evidence indicates that the saturated hydrocarbons were first decomposed to form unsaturated hydrocarbons which then polymerized.

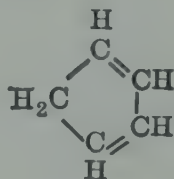
The extent of unsaturation in the monomeric molecule is of considerable importance in determining the ease of polymerization. A compound with two double bonds or a compound with one triple bond polymerizes more readily than a compound with only one double bond. If the double bonds form a conjugated system, as in butadiene, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$, polymerization occurs more readily than it does if the double bonds are farther apart. A compound with two conjugated triple bonds is still more reactive than a compound with two conjugated double bonds. In general, the greater the degree of unsaturation, the greater the ease of polymerization. The same comparisons hold in the case of cyclic unsaturated hydrocarbons, e.g., 1,3-cyclohexadiene polymerizes more readily than cyclohexene. 1,3-Cyclopentadiene which has a five-membered ring, polymerizes more readily than 1,3-cyclohexadiene.



Cyclohexene



1,3-cyclohexadiene



1,3-cyclopentadiene

It is interesting and instructive to examine the formulas of the ethylene derivatives which have proved to be most satisfactory for the production of commercially useful polymers.



vinyl chloride



vinyl acetate



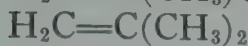
vinylidene dichloride



methyl acrylate



methyl methacrylate



isobutylene



styrene

³ Lind and Bardwell, *J. Am. Chem. Soc.* **48**, 2335 (1926).

Every one of these compounds possesses a CH_2 group linked by a double bond to another carbon atom, $\text{C}=\text{CH}_2$. Except in the field of heteropolymers and coumarone-indene polymers, no useful polymer has yet been obtained from a derivative of ethylene which did not have this fundamental structure.

The effect of various substituents on the polymerization tendencies of olefines and diolefines has been studied. Substitution of a hydrocarbon radical, either alkyl or aryl, on the β -carbon atom of 1,3-butadiene has an accelerating effect on the rate of polymerization. Surprisingly, the heptyl radical has a greater accelerating effect than the methyl radical. Substitution of an alkyl radical on the α -carbon atom of 1,3-butadiene decreases the rate of polymerization. These conclusions are based upon the data found in Table I-3.

TABLE I-3 ^a

Name	Formula	Rate of Polymerization
1,3-Butadiene	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.8
Isoprene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	1.0
2,3-Dimethyl-1,3-butadiene	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{CH}_2$	3
2-Heptyl-1,3-butadiene	$\text{CH}_2=\text{C}(\text{C}_7\text{H}_{15})\text{CH}=\text{CH}_2$	9
2-Phenyl-1,3-butadiene	$\text{CH}_2=\text{C}(\text{C}_6\text{H}_5)\text{CH}=\text{CH}_2$	90
1,3-Pentadiene	$\text{CH}_3\text{CH}=\text{CHCH}=\text{CH}_2$	0.3

^a Carothers, *Ind. Eng. Chem.* 26, 32 (1934).

The introduction of a halogen atom in an unsaturated molecule increases the rate of polymerization tremendously. Ethylene can be polymerized only under relatively drastic conditions, but vinyl chloride polymerizes readily. The ease of polymerization of the vinyl halides is:



Vinylidene dichloride, $\text{CH}_2=\text{CCl}_2$, polymerizes easily, yet trichloroethylene, $\text{CCl}_2=\text{CHCl}$, is quite stable with respect to polymerization. This emphasizes the fact that the structure $\text{C}=\text{CH}_2$ is an important structural configuration for the polymerization of olefines. Still further evidence of the effect of halogens in facilitating polymerization is found in a comparison of the polymerization rates of the halogen substituted butadienes. Substitution on the β -carbon atom has a much greater effect than substitution on the α -carbon atom. As shown in Table II-3, the effect increases, $\text{Cl} < \text{Br} < \text{I}$.

TABLE II-3^a

Name	Formula	Rate of Polymerization
1,3-Butadiene	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	0.8
Chloroprene	$\text{CH}_2=\text{CClCH}=\text{CH}_2$	700
Bromoprene	$\text{CH}_2=\text{CBrCH}=\text{CH}_2$	1000
Iodoprene	$\text{CH}_2=\text{CIHCH}=\text{CH}_2$	1500
2,3-Dichloro-1,3-butadiene	$\text{CH}_2=\text{CClCCl}=\text{CH}_2$	2000
1-Chloro-1,3-butadiene	$\text{ClCH}=\text{CHCH}=\text{CH}_2$	7

^a Carothers, *Ind. Eng. Chem.* 26, 32 (1934).

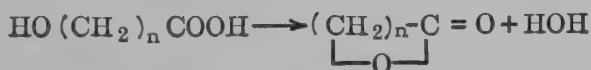
The unsaturation of the carbonyl ($\text{C}=\text{O}$) group found in aldehydes and ketones may give rise to polymer formation. Formaldehyde yields paraformaldehyde, polyoxymethylene or trioxymethylene, depending upon the experimental conditions. Acetaldehyde yields paraldehyde, aldol, and polyaldols. Other aliphatic aldehydes can yield polymers by repeated aldol condensations. Dialdehydes and keto-aldehydes also form polymers. Molecules containing a carbon-carbon double bond conjugated with a carbon-oxygen double bond are particularly susceptible to polymerization. Acrolein, crotonaldehyde and maleic dialdehyde are examples of this class.

Effect of Chemical Structure in Condensation Polymerizations.—When the effect of chemical structure on a *condensation* type of polymerization is considered it is found that the general reactions of fundamental organic chemistry apply. The only requirements for condensation are suitable reaction conditions and proper functional groups. The most common functional groups which are suitable are OH , CHO , COOH , NH_2 , NHR , X (halogen). Combinations of these groups are involved in reactions between phenol and formaldehyde (Bakelite phenolic resins), glycerol and phthalic anhydride (alkyds), diamines and dibasic acids (Nylon), alkyl dihalides and sodium polysulfide (Thiokol).

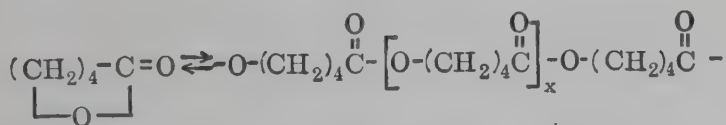
The positions of the reacting groups must be such that the formation of a five- or six-membered ring is impossible. It is a well-known fact that five- and six-membered rings are formed more readily than either smaller or larger rings. According to the Baeyer Strain Theory, there is less strain involved in five- and six-membered rings than in smaller rings and hence compounds containing the former rings should be more stable than those composed of smaller rings. The Strain Theory also predicted that rings with more than six carbon atoms would show decreasing stability, due to the magni-

tude of the strain involved, assuming that all of the carbon atoms are in the same plane. In recent years it has been proved that the carbon atoms of a large ring may lie in more than one plane, and strainless rings containing more than thirty carbon atoms have been prepared. In view of the fact that five- and six-membered rings are formed more readily than rings of any other size, it follows that the terminal groups are closer together in molecules which can form five- or six-membered rings than they are in larger molecules. With increasing size of the molecule there is less and less likelihood that the two ends will meet before a reaction collision with another molecule occurs. A corollary of this fact has been utilized in one of the most successful methods of making large cyclic molecules. In this case, the large straight-chain molecule is used in an extremely dilute solution. The idea is to permit the two ends of the single molecule to react before the functional groups of two molecules undergo a reaction collision. If a polymer is desired from the same straight-chain molecule, however, a solution of high concentration should be used in order to promote intermolecular condensations in preference to intramolecular ring formation.

A comparison of the stability of five-, six-, and seven-membered lactones toward polymerization reactions is instructive. Lactones are formed from hydroxy acids by an intramolecular condensation, e.g.,



Five-membered lactones are very stable and do not change to polymers; six-membered lactones form an equilibrium with the corresponding linear polymer; seven-membered lactones can be changed easily and completely to the linear polymer.



Physical Conditions Affecting Polymerization.—Polymerization reactions are affected by the same physical conditions that cause variations in simple organic reactions. These may be summarized as:

1. Nature and amount of catalyst.
2. Temperature and pressure.
3. Reaction time.
4. Concentration.
5. Solvent.

The effects produced by certain conditions are obvious. The catalyst, for example, acts as the main directive influence and is, therefore, capable of changing the course of the reaction. When combined with high temperatures, large amounts of effective catalysts produce a rapid reaction and accordingly cause the formation of polymers of low molecular weight. When the amount of catalyst and the temperature are regulated to produce a moderate reaction requiring a longer period of time, the molecular weight of the product is raised.

These conditions by which the molecular weight of the polymer may be altered can be easily explained by a consideration of the physical mechanism involved in the growth of the chain. With a high concentration of catalyst and at an elevated temperature, a multitude of monomeric units start the conversion to polymer with the result that many small polymers are formed in a very short period of time, and practically all of the monomer is used up before any large molecules can be formed. When only a few reaction centers are created by suitable conditions, the probability of these growing to form large molecules is increased.

When a polymerization reaction is carried out in solution, it is a general rule that the higher the concentration, the greater the molecular weight of the product. (See Table III-3). This is due to the larger number of effective collisions which can occur when the monomeric units are close to each other. The actual limit to which this rule holds must be determined for each reaction. Various effects such as the viscosity produced and the temperature control (if the reaction is exothermic) must be considered in determining the optimum concentration in a particular reaction.

TABLE III-3. CONCENTRATION EFFECT: METHYL METHACRYLATE
POLYMERIZED IN METHANOL-WATER SOLUTION ^a

Monomer (Per Cent)	Induction Period (Hours)	Molecular Weight (in Thousands)
5	45	100
10	21	140
20	18	168

^a Strain, *Ind. Eng. Chem.* 30, 347 (1938).

The great effect of concentration on molecular weight has been demonstrated by determining the molecular weight of the product at

various stages of a polymerization experiment. It has been found, in the polymerization of methyl methacrylate, that the molecular weight of the product decreased progressively during the reaction as the monomer was used up. These values are recorded in Table IV-3.

TABLE IV-3. EFFECT OF MONOMER CONCENTRATION IN BENZENE ON YIELDS AND MOLECULAR WEIGHTS OF POLYMER ^a

Per Cent Monomer	2 Days		17 Days		74 Days	
	Per Cent Yield	Mol. Wt. $\times 1000$	Per Cent Yield	Mol. Wt. $\times 1000$	Per Cent Yield	Mol. Wt. $\times 1000$
2	0.0	—	0.0	—	0.0	—
5	0.0	—	0.0	—	3.0	26
10	0.5	—	5	36	59.0	33
20	21.0	95	60	62	70.5	52

^a Strain, *Ind. Eng. Chem.* **30**, 347 (1938).

The nature of the solvent also causes variations in the product. The molecular weight of the polymer may be altered as a result of the specific effect many solvents have upon the speed of a reaction. Also, in a few cases, it has been found that a certain type of solvent favors the formation of a cyclic compound in preference to a linear polymer.

Experimental Techniques.—The four general methods used in carrying out a polymerization reaction are:

1. Mass or bulk polymerization.
2. Solution polymerization.
3. Gaseous or vapor phase polymerization.
4. Emulsion polymerization.

Mass polymerization is the term applied to the polymerization of liquid monomers without the addition of any diluent. Styrene, acrylates, indene, and butadiene are compounds which are often polymerized by this method. As a general rule, atmospheric pressure and elevated temperatures are used, but in the polymerization of isobutylene a low temperature is preferable. If the polymer is soluble in the unreacted monomer, as it usually is, the course of the reaction can be followed by determining the increase in the viscosity of the liquid at definite intervals of time. Other methods of measuring the rate of polymerization are to determine the progressive change in freezing point, refractive index, absorption spectra; or to

determine the amount of unchanged monomer by distillation or extraction methods. When the polymer is insoluble in the excess of monomer, the course of the reaction can be followed by measuring the amount of precipitate formed in a given period of time. The amount of by-product, e.g., water, ammonia, or salt, formed as a result of a condensation polymerization, is a convenient measure of the reaction speed in such cases.

Solution polymerization results when the monomer is first dissolved in a suitable solvent. The same general characteristics associated with mass polymerization are found in solution polymerization. However, it is usually possible to obtain better control of temperature and of reaction speed in solution polymerization than in mass polymerization.

Gaseous polymerization is simply a polymerization carried out in the gaseous or vapor phase. It is usually done at an elevated temperature and under pressure. In this way, ethylene can be polymerized to form a waxy solid known as Polythene.

The most fascinating and apparently the most satisfactory method is emulsion polymerization, which consists in causing polymerization of the unsaturated organic compound present as the oil in an oil-in-water emulsion. It is by this means that the highest molecular weight types may be produced, with excellent control of conditions and therefore, with the greatest possibility of obtaining reproducible polymers. The most interesting and the most useful polymers formed by this means are the synthetic rubbers of the Buna type. Since gaseous 1,3-butadiene is the principal reactant, these emulsion polymerizations are performed under pressure.

Nine basic ingredients have been cited by Mark and Raff⁴ as necessary for an emulsion polymerization.

1. *Basic phase*: the continuous phase of the emulsion representing 60–80% of the total weight of the system. This is usually water, freed from all inorganic impurities.

2. *Main monomer*: the principal component of the reaction if copolymerization is involved. Typical examples are butadiene or vinyl chloride. This monomeric material represents 60–80% of the final polymer or 15–30% of the emulsion.

3. *Additional monomers*: the monomer which copolymerizes with the main monomer. Typical examples include vinyl acetate, styrene, acrylates, or acrylonitrile. One of the principal ways in which the

⁴ Mark and Raff, *High Polymeric Reactions, High Polymers*, Vol. III, p. 81, Interscience Publishers, Inc., New York, 1941.

properties of a polymer may be altered is by changing the ratio of main and additional monomers used in the polymerization procedure. This material accounts for 20–40% of the final polymer or 5–15% of the emulsion system.

4. *Emulsifying agent*: required for the production of colloidal dispersions. Great care is necessary in the selection of the proper agent in each reaction. Conditions of both type and amount markedly influence the stability of the dispersion. Typical agents commonly applied include carboxylic and sulfonic acid soaps, rosin soaps, sulfonated long-chain alcohols and amines. The amount usually ranges from 0.2–2% based on the weight of the final polymer. The value, however, may be as high as 5%.

5. *Stabilizer*: a protective colloid used to prevent the “breaking” or precipitation of the colloidal dispersion. Typical materials as glues, casein, starch, or water-soluble resins may be used in amounts ranging from 2–5% of the polymer weight.

6. *Surface tension regulator*: serves the purpose of regulating the size of the colloid particles within narrow limits. Aromatic alcohols, aliphatic alcohols (C_5 to C_8), and aromatic amines have been recommended for use between the limits of 0.1%–0.5% of the polymer.

7. *Catalyst*: specific agent for accelerating the formation of polymerization nuclei. An excess of catalyst also speeds up the cessation of the reaction and may produce low molecular weight products. Oxidizing agents as ozone, oxygen, persulfates, peroxides, and perborates are representative of those used in amounts ranging from 0.1%–1% of the polymer.

8. *Regulator*: little is known of the influence of these agents. They appear to have a directing effect on the reaction and, particularly, tend to decrease the amount of cross-linking or side-chain reaction which may occur. Chlorinated aliphatic compounds such as carbon tetrachloride and hexachloroethane are useful in most cases. Amounts ranging from 2–5% of the polymer are used.

9. *Buffer*: the pH of the emulsion must be rigorously maintained for proper stability. Phosphates, carbonates, and acetates are used for this purpose to the extent of 2–4% of the polymer.

The exact purpose or role of many of the ingredients is not yet clearly understood. The mechanism of the reaction is complicated and dependent upon a variety of conditions. The multiplicity of products which may be obtained by variations in the ingredients used is very great.

Review Questions

1. What types of organic reactions are involved in polymerization processes?

2. Explain each of the terms:

addition
copolymerization
functional group
heteropolymerization.

3. Which of the following combinations could be used to produce a polymer:

benzoic acid + ethylene glycol
phthalic acid + ethylene glycol
phthalic acid + butyric acid
phthalic acid + glycerine
8-hydroxyoctanoic acid
ethyl chloride + sodium tetrasulfide
 β,β' -dichlorodiethyl ether + sodium tetrasulfide
ethylene diamine + adipic acid
diethylamine + adipic acid?

4. Arrange members of each of the following groups in the order of increasing reactivity in polymerization:

- (a) ethylene, ethane, 1,3-butadiene, 1,5-hexadiene, 1-hexene.
- (b) isoprene, bromoprene, 2-heptyl-1,3-butadiene, 1-chloro-1,3-butadiene, 1,3-butadiene, iodoprene.
- (c) tetrachloroethylene, ethylene, vinyl chloride, vinylidene chloride, 1-chloro-1-butene.

5. What is the greatest advantage of emulsion polymerization? What is the purpose of:

- (a) stabilizer
- (b) emulsifying agent
- (c) regulator
- (d) buffer?

6. What is the effect on molecular weight of the product of:

- (a) high temperature
- (b) concentration
- (c) high percentage of catalyst?

What is the reason for each?

CHAPTER IV

MECHANISM OF POLYMERIZATION

Before discussing the detailed mechanism of the chemical reactions leading to the formation of polymers, it will be desirable to discuss the three types of polymers which can be produced. Both addition and condensation type polymerizations may be used to form these types, which are referred to as:

1. Linear (or chain) polymers.
2. Branched linear (or net) polymers.
3. Cross-linked (or space) polymers.

Differences in the chemical composition of the monomers and differences in the operating conditions used for polymerization are the fundamental causes of the existence of the three general types of polymers. They differ from each other in the atomic arrangements found in the polymer and in the relation which certain parts of a macromolecule have to other parts of the same molecule or to neighboring molecules. Each type of polymer has its own peculiar characteristics or variations by which it may usually be recognized. Much of the problem of providing a mechanism to explain polymerization revolves about an attempt to explain the formation of one type in preference to the others.

Linear Polymers.—As the name implies, linear polymers are simple chains of atoms built by either addition or condensation reactions. The orientation of atoms along such a chain is based upon the fundamental principles of organic chemistry. The usual inter-atomic angles and distances are found in such a chain and are of value in determining the exact configuration of the large molecule. Thus, the "chain pictures" of such complex molecules as rubber, cellulose, starch, and protein have been deduced from a combination of physical measurements, chemical reactions, and analogies to simpler compounds. By the use of such methods, the structure of rubber has been differentiated from that of gutta-percha. Although both of these are built upon the same monomeric unit, isoprene, they differ markedly with respect to such properties as elasticity, hardness, crystallinity, solubility, and moldability.

tion, in most cases, do the molecules become aligned sufficiently to permit a crystalline arrangement. This fact of incomplete alignment accounts in part for the possibility of portions of molecules forming micelles. It may happen that in any plastic body some portion of a chain molecule may be so related to its neighbors that a micelle may be produced. Part of the molecule may take part in micelle formation; i.e., a fraction of the chain may become associated with portions of neighboring chains, while the rest of the molecule remains in an unbound condition. Micelle formation in cellulose is represented diagrammatically in Figure 9.2, p. 153.

The ability of linear polymers to be converted from the amorphous state to the crystalline form by mechanical processing (as stretching) illustrates another fundamental characteristic of this class. This change is due to the mobility of the molecules relative to each other. Thus, rubber in the normal state shows completely amorphous characteristics, but, when stretched, the crystalline form is produced. X-ray study has demonstrated the existence and relationship of these forms. The fibrous nature when stretched, chilled, and ruptured is shown in Figure 4.1.

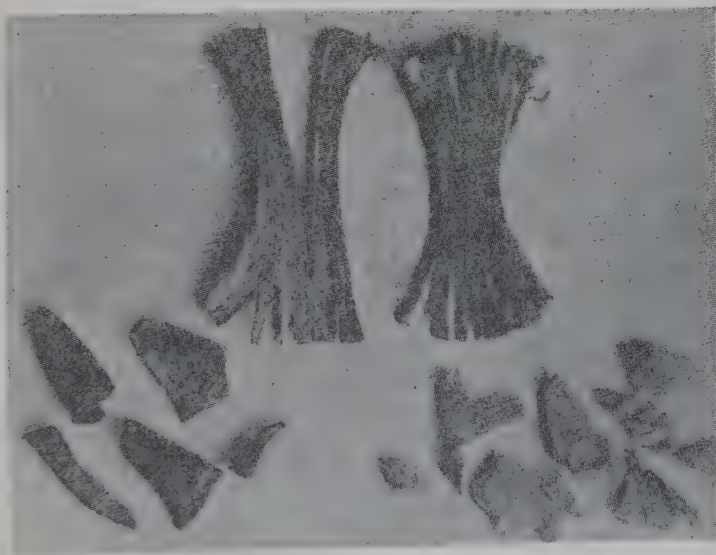


FIG. 4.1. Fibrous rupture of stretched rubber cooled in liquid air.
(Hock, *Z. Electrochemie* 31, 404, 1925.)

Branched Linear Polymers.—This type of macromolecule may be produced by any of the reactions which ordinarily lead to the formation of a linear polymer. In an addition type of polymerization, branching of the linear chain is due to the formation of an open

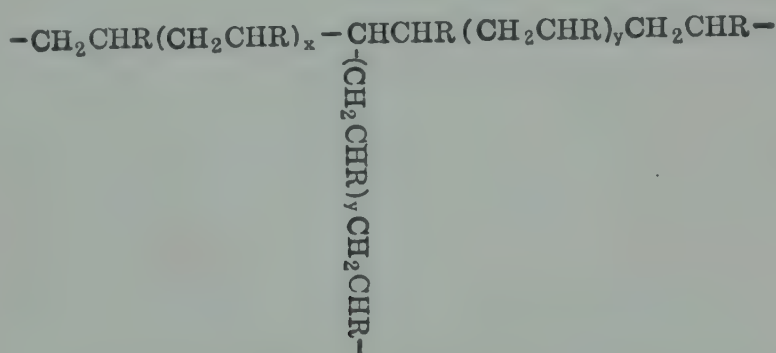
position along the chain. For example, in the formation of a linear polymer from an olefine, according to equation (4.1),



disproportionation may occur between two molecules of olefine as in equation (4.2).



The $\underset{\text{|}}{\text{CH}}=\text{CHR}$ radical can not only find its place in the linear chain, but it can also start a branched chain, giving rise to the following type of molecule:



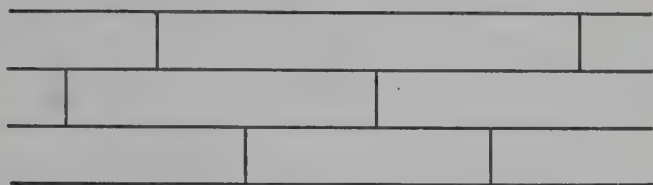
Since this type of branching may occur at different parts of the chain and since it is also possible that an open position may occur on a side chain, a general graphical representation of this type of polymer is as follows:



If there are two or more functional groups in a molecule of monomer used for addition polymerization there is a possibility of forming either a branched linear polymer or a cross-linked polymer. In the case of condensation polymers, the existence of three functional groups in one of the reactants will result in the formation of branched linear polymers or, more frequently, cross-linked polymers.

Cross-linked Polymers.—The cross-linked polymeric molecules differ from the branched linear macromolecules in that the ends of the branches are not free, but are linked chemically to another long,

linear molecule. This type of polymer can be represented graphically by the following diagram:



In this type of polymer, the constituent parts are all tied together to form a relatively rigid structure. The physical properties of cross-linked polymers, particularly their insolubility and infusibility, are very different from the physical properties of linear polymers. Branched linear polymers really constitute an intermediate class between linear and cross-linked polymers. If the branching is not extensive, they resemble linear polymers in their characteristics. However, with increasing size and complexity of the branched chains, and consequently greater interference in the movements of neighboring molecules, these branched linear polymers become more and more like the cross-linked polymers. Poor fusibility and low solubilities relate the highly branched molecules to the cross-linked types.

MECHANISM OF POLYREACTIONS

It should be stated at the beginning of this discussion that our knowledge of the mechanisms of the reactions by which polymers are produced is very limited. Various theories and postulates have been presented and some experimental evidence has been obtained to support them, but the picture is still far from complete. The principal reason for the slow progress made in this field is the size and complexity of polymeric molecules. A large number of organic chemists in the past have veered away from a detailed study of amorphous substances of high molecular weight and have devoted their time and skills to the preparation and properties of crystalline solids.

From what has been discussed previously, it is easy to realize that from the very nature of a polymerization reaction, there is no fixed point at which a polymer chain will stop growing. That depends, to a large extent, on the operating conditions employed. Even under the same operating conditions, however, there is no *a priori* reason to expect every polymeric chain to reach the same dimensions before all of the monomer has been used. The worker in this field is confronted, not with a pure substance composed of large

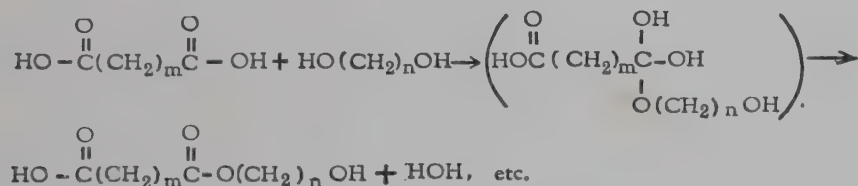
molecules, but with a material which is a mixture of large molecules of quite different molecular weights. Even if the molecules were all of the same size, it would be impossible to determine the molecular weight by means of the usual methods of freezing-point lowering or boiling-point elevation. For example, if a polymer has a molecular weight of 20,000, it would be necessary to dissolve 400 grams of it in 1000 grams of benzene in order to produce a lowering of the freezing point of 0.1°C . Other difficulties encountered are the colloidal characteristics of solutions of the polymers, the dwarfing of the activity of functional groups as a result of the immense size of the molecule, the saturation of the terminal valences, and the determination of stereoisomeric configurations. New and ingenious techniques have been developed in order to overcome these difficulties. Some of these techniques will be discussed in Chapter VI.

All reactions resulting in the formation of polymers involve a chemical reaction between two or more molecules. These molecules may be identical, as in the case of simple addition polymerization, or they may be different, as in the case of copolymerization and most condensation polymerizations. In order for any reaction to occur between two molecules, it is necessary for them to collide with each other. Since no reaction can occur without a collision, it is obvious that the more collisions there are in a given period of time, the more reactions are likely to occur. Consequently, the number of collisions is primarily a function of the concentration of the reacting molecules. However, not all collisions result in a reaction. A certain minimum activation energy or energy of reaction is necessary in order to cause a reaction between the colliding molecules. This energy of activation may be provided by increasing the kinetic energy of the reacting molecules by means of heat, or it may be achieved by means of a catalyst.

Another important factor in determining the number of effective collisions is the average size of the reacting molecules. This consideration is much more important in polymerization reactions than in reactions involving small molecules. As polymerization proceeds, increasingly large molecules are formed which have reactive, functional groups at one or both ends of the chain. In order for the polymer chain to grow, a small molecule must collide with this large molecule at, or at least very near, the functional group at the end of the chain. For example, in the formation of a polyester from a glycol and a dicarboxylic acid, there may be formed a large molecule with an hydroxyl group on each end. The next step in the polymerization involves a reaction between this hydroxyl group and the

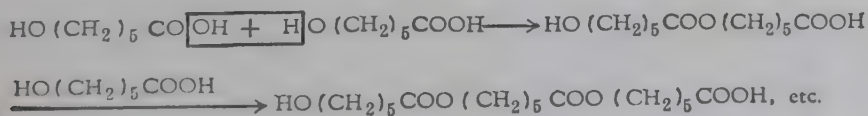
carboxyl group of a molecule of acid. For an effective collision, the acid molecule must collide with the large molecule in such a way that the carboxyl group is in close proximity to the hydroxyl group. If the acid molecule collides with any other part of the large molecule, no reaction occurs. It is obvious, then, that as the size of a macromolecule increases, the number of effective collisions with another molecule decreases, and hence the speed of the reaction decreases.

Condensation Polymerizations.—In polycondensations, the reaction proceeds in a stepwise fashion. The fundamental reactions involved in each step are repeated many times in building up the polymer. Such terms as polyesterification, polyetherification, and polydehydration are descriptive of the reaction involved at each step in the growth of the chain. The detailed mechanism of each of these reactions is the same as that involved in the interaction of simple molecules, each containing only one of the reacting groups. The reactions are usually intermolecular reactions, e.g.,

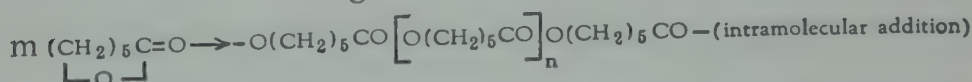
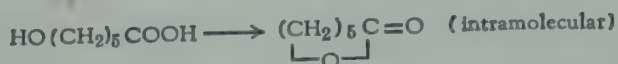


The factors discussed under reaction rates, namely, the number of collisions and the energy of activation, have an important bearing on the speed with which a given polymerization proceeds. Regardless of whether the reaction is carried out with or without an inert solvent, the frequency of collisions decreases as the amount of polymerization increases. Furthermore, as the size of the molecule increases, the possibility of effective collisions decreases because of the decreasing likelihood of the reactive functional groups colliding. Finally, the energy required for the activation of a large molecule is probably greater than that required for a small molecule. The same experimental conditions which cause a fairly rapid reaction between small molecules may result in a very slow reaction rate when one of the reacting molecules is large. Sluggishness and decreased speeds result, therefore, as the polymer grows. Three possible mechanisms may be proposed for condensation reactions.

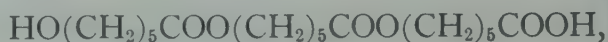
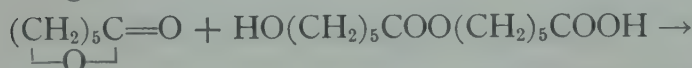
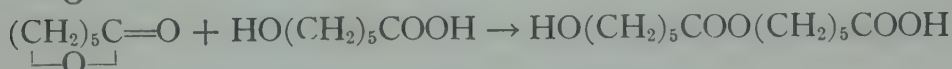
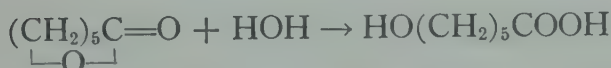
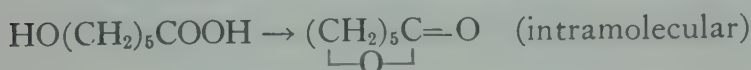
1. Simple intermolecular condensation. This is undoubtedly the mechanism involved in most condensations.



2. Intramolecular reaction followed by intermolecular addition. In the polymerization of an hydroxy acid, a possible mechanism is the formation of a cyclic lactone followed by a combination of these lactone molecules to form a linear polymer.



3. Intramolecular reaction followed by addition of water to the cyclic compound formed and subsequent intermolecular addition. Using 6-hydroxyhexanoic acid again as an example, the lactone may be formed by an intramolecular dehydration. A trace of moisture may then react with some of the lactone molecules, regenerating the hydroxyacid which could then add to the lactone, e.g.,



etc. (intermolecular)

It is, of course, possible that not all of the hydroxy acid is changed to the lactone form. The polymer could be formed by the reactions indicated in the last two equations. Even when the lactone is isolated prior to polymerization, the third mechanism seems more plausible than the second, as the merest trace of water would be sufficient to start the reaction. It is interesting to note that the polymerization of the cyclic ethylene oxide has been shown to involve the preliminary formation of a small amount of ethylene glycol by the addition of water, followed by the addition of the glycol to ethylene oxide.² The glycol thus formed can add to another molecule of ethylene oxide. This intermolecular addition reaction can continue in stepwise fashion until the macromolecule is formed.

Addition Polymerizations.—The mechanism by which addition polymers are formed is generally much more complex than that involved in the formation of condensation polymers. The first step in an addition polymerization is activation of the monomeric

² Perry and Hibbert, *J. Am. Chem. Soc.* 62, 2599 (1940).

molecule. This activated molecule then reacts rapidly with other monomeric molecules and finally the reaction stops, due to the loss of activity of the large molecule. These three steps comprise the essential changes involved in a chain reaction. Each of these steps will be discussed in some detail.

Activation of the Monomer.—There are three general methods of activating the monomer, namely, by the addition of heat, light or a catalyst. Regardless of the means of activation, the high reactivity of the activated monomer is due to an increase in its energy content. This excited molecule is the nucleus from which the polymer chain grows. As yet, there is no general agreement concerning the exact nature of the activated monomer.

According to some investigators the excitation may consist of an activation of the double bond, e.g.,



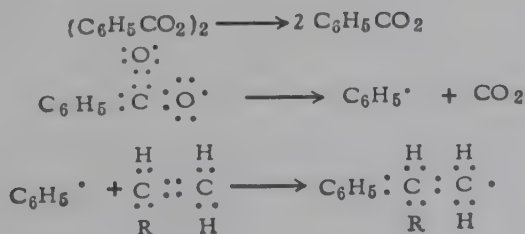
where K represents the energy required for activation and $\text{RCH}=\overset{*}{\text{CH}}_2$ represents the activated monomer. This type of activation is characterized by activation energies of the order of 20,000 calories per mole, a relatively long life period for the activated nucleus, and relatively slow chain growth.

A second method of representing the activated monomer is to assume the formation of a biradical, e.g.,



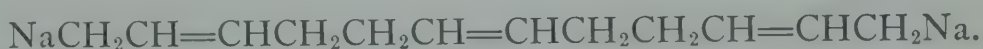
This type of activation is characterized by activation energies of the order of 25,000 calories per mole, a short life period for the activated nucleus and rapid chain growth. The activation energies determined for many polymerization reactions do not clearly indicate the nature of the nucleus formed. It is, of course, perfectly possible for both types of nuclei to be formed in the same polymerization reaction.

When a catalyst such as benzoyl peroxide is used as a means of excitation, it has been postulated that the benzoyl peroxide decomposes to yield a free phenyl radical which combines with the monomer to form a new free radical, e.g.,



In this case, the activated monomer is actually combined with a radical obtained from the catalyst. If this mechanism is correct, the phenyl radical should be found in the polymer molecule. When *p*-bromobenzoyl peroxide was used as a catalyst for the polymerization of styrene, the polymer molecules were found to contain bromine.³ This constitutes excellent evidence in support of the free-radical mechanism for polymerizations catalyzed by peroxides.

When metallic sodium is used as a catalyst, it is believed that the monomer is activated by the formation of an organo-sodium compound. For example, it has been postulated that the first step in the polymerization of butadiene with sodium is the formation of $\text{NaCH}_2\text{CH}=\text{CHCH}_2\text{Na}$. This compound is assumed to add to two molecules of butadiene to form



This process may be repeated until a high molecular weight polymer has been formed. Experimental support for this mechanism is found in the fact that organo-alkali compounds which do not add to olefines do not catalyze polymerization.⁴

Chain Growth.—The reaction by which the polymer chain is built up proceeds more readily and more rapidly than the activation of the monomer. The activation energies involved are of the order of 5000 to 8000 calories per mole, and correspond to those that would be expected if the reaction is due to free radicals or activated molecules. The actual mechanism by which the chain grows is dependent upon the nature of the activated monomer.

When the excited monomer molecule contains an activated double bond, it is believed to add to an unactivated molecule by a simple *HX* addition, e.g.,



This activated molecule may add to another molecule of monomer and the process may be repeated as long as the molecule retains a sufficiently active double bond at its growing end. When this mechanism is involved, chain growth is slow and the active chains have a relatively long life. Furthermore, this type of chain growth is relatively insensitive to temperature changes and to small amounts of impurities.

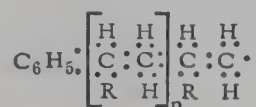
³ Price, Kell and Krebs, *J. Am. Chem. Soc.* **64**, 1103 (1942).

⁴ Gilman, *Organic Chemistry, An Advanced Treatise*, Vol. I, 2nd ed., p. 528, John Wiley & Sons, Inc., New York, 1943.

If the activated monomer molecule is of the biradical type, it may add to an unactivated molecule to form a new biradical, e.g.,



This new biradical may add to another molecule of monomer and the process may be repeated indefinitely. In this case, chain growth is rapid, the activated nuclei have a short life period, and the reaction is sensitive to slight variations of temperature and to small amounts of impurities. The characteristics of the peroxide-catalyzed polymerization are similar to those of the biradical type. Each newly-formed free radical adds to a monomer molecule until something happens to stop the chain growth. The intermediate radicals may be represented by the general formula,



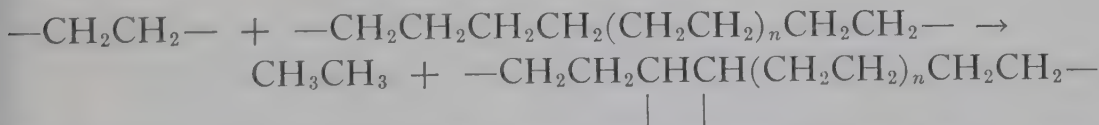
In discussing each of the mechanisms described above, it was stated or implied that chain growth occurred by the addition of one molecule of monomer at a time. It is, of course, possible that two chains of varying size may combine to form a much longer chain. The extent to which such a reaction is involved in polymer formation has not been determined, but it may account for a large proportion of the high molecular weight polymers formed under certain conditions.

On the other hand, a collision between two activated chains may be accompanied by an exchange of activation resulting in the formation of branched polymers. This may be represented as follows:



One of the resultant chains has three open positions or directions in which chain growth may continue, with the formation of a branched polymer.

Open positions may also result from the collision of an activated nucleus with a long chain, e.g.,



Cross-linking may result from the simultaneous formation of open positions on adjacent chains.

There are three possible ways in which the monomeric molecules may unite in forming a linear polymer. The most prevalent of these is described as a "head-to-tail" arrangement and can be represented as follows:



This is the way in which such monomers as styrene, isobutylene, vinyl esters and most of the acrylic esters have been found to polymerize. A second possibility is a "head-to-head" and "tail-to-tail" arrangement, e.g.,



This arrangement has been found in the polymers obtained from α -halogen acrylates. The third possibility is a purely random arrangement including head-to-tail, head-to-head and tail-to-tail groupings, e.g.,



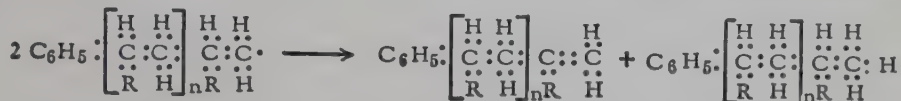
Cessation of Chain Growth.—The factors involved in the cessation of the growth of a polymer chain are of great importance in controlling the size of the molecules formed. The kinetic factors of collision frequency, steric hindrance and activation energy, and their changes during chain growth have been discussed earlier (p. 42). In addition to these factors, there are specific reactions which may cause a stoppage of the growth of macromolecules.

One of the earliest theories proposed to explain cessation of chain growth was based on the idea of mutual saturation of the free valences existing at the growing ends of the chain. This could be accomplished either by the mutual saturation of the two ends of a single chain or by the mutual saturation of the ends of two parallel chains. In either case a cyclic compound would be formed. It has been pointed out earlier (p. 30) that ring formation from a single molecule is highly improbable in polymerization reactions under the conditions generally used. Ring formation from the mutual saturation of two chains of approximately the same size seems a little more likely to occur. The behavior of such a compound would be expected to resemble rather closely that of two independent chains lying side by side. However, there is no evidence to support this theory of growth cessation.

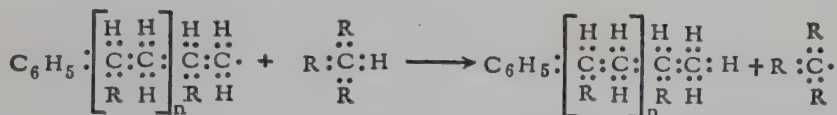
A general explanation for cessation of chain growth involves loss of activation during collision with another molecule. There are several ways in which this may occur.

1. The growing chain ends may become saturated with foreign molecules such as solvent, catalyst, or inhibitor.⁵ It is a well-known fact that the addition of small amounts of inhibitors will cause a polymerization reaction to cease.

2. Two active chains may collide in such a way that one chain loses a hydrogen atom and the other acquires a hydrogen atom, e.g.,



3. An active chain may acquire a hydrogen atom from some other molecule present in the reaction mixture. While this would cause cessation of chain growth, the molecule from which the hydrogen atom was obtained would become a free radical and could serve to activate another molecule of monomer.



4. If growth cessation occurs by the acquisition of a hydrogen atom from a growing chain, branching may occur (see p. 40).

5. Another possible explanation for the stoppage of chain growth is by isomerization of the growing chain. This may occur as a result of the migration of a hydrogen atom, e.g.,



This results in the formation of a typical double bond. In most cases, the polymers formed do not exhibit any olefinic characteristics such as bromine absorption or hydrogenation. This may well be due to the experimental difficulties involved in detecting a single double bond in a molecule whose molecular weight is of the order of 50,000.

Distribution Curve.—Ordinarily, in a polymerization reaction, molecules are produced which have the same empirical formula but different molecular weights. In general, a small proportion of the

⁵ An inhibitor is a substance which causes a chain reaction to cease, usually after a few molecules have reacted. In some cases, the inhibitor appears to prevent the reaction completely, at least for a long period of time.

molecules have a relatively low molecular weight, a small proportion have a relatively high molecular weight, while the majority of the polymeric molecules lie between these two extremes. The amounts of high, low, and intermediate molecular weight products are conveniently expressed by means of a distribution curve. The data necessary for plotting a distribution curve are obtained by fractional separation of the polymer molecules, making use of the different solubilities of the molecules of different molecular weights. The average molecular weight of each fraction is then determined. The

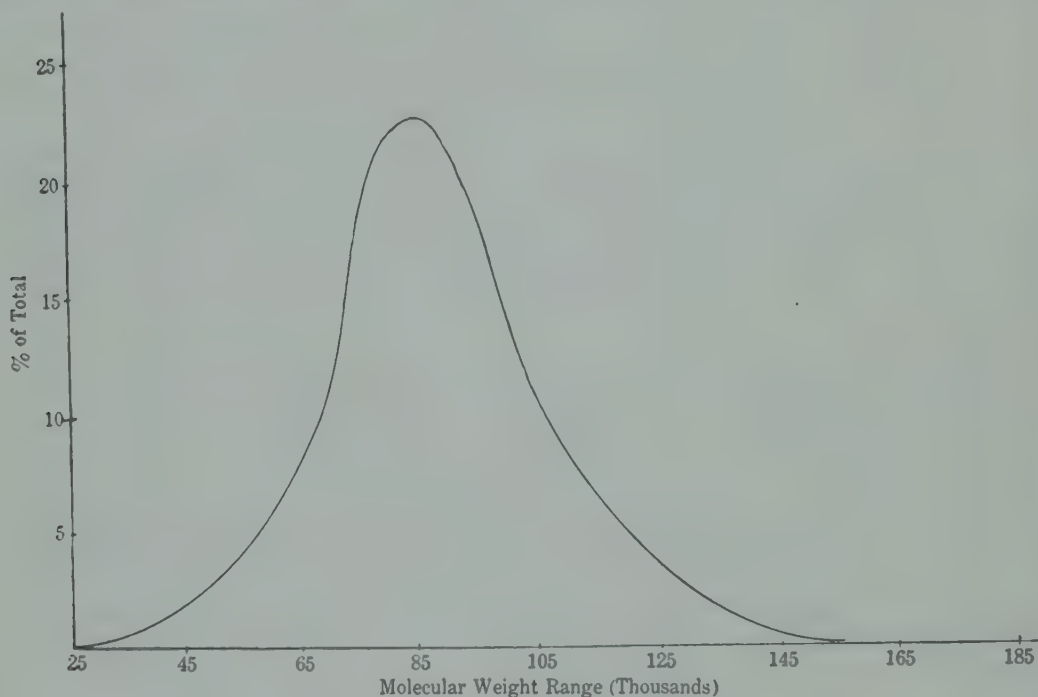


FIG. 4.2. Graph showing distribution of molecular weight.

percentage of the total polymer found in each fraction is plotted against the corresponding molecular weight to give the distribution curve. Table I-4 shows the experimental results obtained by Signer and Gross with a polystyrene whose average molecular weight was 80,000. Figure 4.2 shows the distribution curve obtained by using the data in Table I-4.

The exact shape of the curve, in the case of addition polymerization, is determined principally by the interrelationships of the three phases involved, namely, activation of the monomer, chain growth and cessation of chain growth. For example, if the reaction by which chain growth proceeds is relatively rapid in comparison with the initiation and cessation reactions, the centers of activation grow

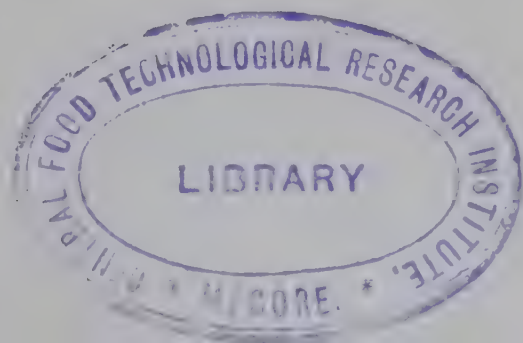
TABLE I-4^a

Per Cent of Total	Molecular Weight Range
0.2	25- 35,000
1.7	35- 45,000
3.6	45- 55,000
8.4	55- 65,000
20.0	65- 75,000
23.8	75- 85,000
20.2	85- 95,000
10.4	95-105,000
6.0	105-115,000
3.3	115-125,000
1.7	125-135,000
0.5	135-145,000
0.2	145-155,000

^aSigner and Gross, *Helv. Chim. Acta*, **17**, 726 (1934).

rapidly to a very great length before new centers are generated or before the chain-stopping mechanism interferes. The product of such a reaction consists of a large proportion of high molecular weight molecules and a minimum of smaller molecules. Such a product may be expected when free radicals initiate the polymerization reaction. On the other hand, if the activation reaction is more rapid than either the growth or cessation reactions, many growth centers are produced in the reaction mixture and many chains grow simultaneously. Consequently there is considerable competition for the available supply of monomeric molecules needed for chain growth. When this situation occurs, the product may consist largely of polymers having low molecular weights. However, the actual size of the polymers depends upon the relationship between the speeds of the growth and cessation reactions. As the speed of the growth reaction increases relative to the speed of the cessation reaction, the chain length becomes greater, and vice versa. This type of polymerization is expected when the double bond is activated and chain growth proceeds by actual addition to the double bond.

It should be mentioned that distribution curves can also be plotted for condensation polymerization reactions as well as for addition polymerizations.



Review Questions

1. Why is the structure of the polymer dependent upon the number of functional groups in the monomers?
2. Explain linear, branched, and cross-linked molecules and the conditions leading to the formation of each.
3. What differences in physical properties exist between the linear and cross-linked polymers?
4. What factors are important in the determination of "effective collisions"? Reasons.
5. What is the radical theory of addition polymerization? What is the "intermolecular theory" of condensation polymerization?

CHAPTER V

PLASTIC PROPERTIES AND THEIR RELATION TO CHEMICAL STRUCTURE

The plastics industry may be described as consisting of two separate divisions. The first of these deals with the synthesis or production of the basic resinous material. In this field, the synthetic organic chemist plays a most important part. For the actual fabrication of plastic materials and appliances, the services of chemical and mechanical engineers are required. Between these two branches of preparation and application lies the hinterland of the development chemist. It is he who is concerned with the determination, testing and study of plastics properties and behavior characteristics. This phase of the plastics industry is unusually complicated because of the many factors which may affect the ultimate physical characteristics of the plastic body. The proper choice of a serviceable plastic in a particular application requires a considerable amount of experimentation and study. The four principal steps which must be taken by a chemist who is faced with the problem of selecting a plastic which will be suitable for a particular use are as follows:

1. Determination of the essential characteristics required of the finished product.
2. Selection of the resin and the compounding agents, i.e., other materials added to the resin to improve properties or to aid in processing.
3. Selection of the most favorable method and conditions of fabrication.
4. Determination of performance characteristics under all conditions of service.

The magnitude of such an undertaking explains readily why one of the chief concerns of the plastics industry is to summarize and correlate physical data. The workers in this field are particularly interested in any possible correlation of physical characteristics with those of chemical structure. The problem has many ramifications but already numerous correlations have been pointed out well enough to permit their use in prediction of behavior in other cases.

The essential requirements which must be set forth for each application can be most conveniently discussed according to their position in one of the five principal classes:

1. Mechanical properties.
2. Thermal properties.
3. Electrical properties.
4. Optical properties.
5. Chemical properties.

Certain precautions should be mentioned before discussing these specific properties. First, the beginner in the plastics industry should learn to accept the recorded numerical values only as averages of what may be obtained by use of that plastic. The effect and number of possible variables in any plastic formulation is great. The method of compounding, the ingredients used, the history of the plastic used, the exact processing procedure, all lead to variations in the values of a plastic's physical properties. Data recorded in the literature should be studied objectively and should be considered as an indication of what may be obtained under a given set of conditions.

Before discussing the effect of various factors on the physical characteristics of plastics, the basic ideas concerning the structure of macromolecules should be reviewed. It will be recalled that the polymeric body is composed of linear, branched, or cross-linked chains, each chain being held together by primary valence forces and each chain being attracted to its neighbors by secondary valence forces. The secondary type of valence depends entirely upon the nature, number and position of the groups present in the chain. This strong intermolecular attraction results in the formation of molecular aggregates or micelles under certain conditions. The possibility of having either single chains or aggregates of chains causes additional difficulty in predicting the behavior of high molecular weight polymers.

MECHANICAL PROPERTIES

When the field of plastics is mentioned, the feature of high strength characteristics combined with low unit weights for most plastic types comes to mind. The combination of the conditions outlined by the terms "strength" and "weight" comprises the field of mechanical properties.

Weight.—For comparison, the unit weight is expressed by the *specific gravity*. The plastic bodies, alone, are relatively light materials and are of particular interest in the production of airplanes

because of this feature. As expected, the values of unit weight are dependent on the chemical type being investigated and on the relative proportions and individual specific gravities if a mixture is involved. In the investigation of specific gravity of a compounded plastic, knowledge of the specific gravity and percentage composition of each component makes it possible to calculate the specific gravity of the finished product. In other words, the effect is additive:

$$(\% \text{ resin} \times \text{sp. gr. resin}) + (\% \text{ filler} \times \text{sp. gr. filler}) + (\% \text{ plasticizer} \times \text{sp. gr. plasticizer}) = \text{sp. gr. finished piece.}$$

In a correlation of chemical structure with specific gravity, however, the effect of various substituent groups must be considered. Specific gravity is a constitutive property and hence is dependent not only upon the number and kind of atoms present but also upon the specific arrangement of those atoms in the molecule. For purposes of comparison, Table I-5 illustrates the specific gravities of certain plastics and a few typical metals:

TABLE I-5. SPECIFIC GRAVITIES OF METALS AND PLASTICS

Aluminum	2.67	Cellulose Acetate	1.27-1.63
Magnesium	1.76-1.83	Cellulose Nitrate	1.35-1.60
Brass	8.4	Ethyl Cellulose	1.14
Bronze	8.8	Polymethyl Methacrylate	1.18
Steel (cast)	7.81	Urea-formaldehyde	1.45-1.50

An important consideration in the fabrication of a compounded plastic is the *bulk factor*. This is the ratio of the volumes of a given weight of the unmolded powder and the molded object. Excessively high ratios may cause difficulty in molding.

Of particular emphasis in the consideration of plastic weight as compared to that of metal weight, are the comparative values of strength per unit weight. The combined characteristics of high strength and low weight have made plastic materials favorites in many fields.

Tensile Strength.—The strong primary valence bonds coupled with powerful secondary valence intermolecular forces in plastics result in high tensile strengths of fabricated plastic bodies. This property may be defined as the force necessary to stretch a strip of the plastic being tested to its breaking point. The values representing this property are expressed in pounds per sq. in. A typical machine used for determining the tensile strength of a plastic strip

is illustrated in Figure 5.1. The plastic strip is held between jaws, the lower jaw is pulled downward at a uniform rate. The resulting stress applied to the upper jaw is registered on the scale at the top of the machine or indicated by the recording pen at the upper left of the picture. The tensile strengths of several plastics are represented graphically in Figure 5.2, in which the range of values are shown by the solid areas. For comparison, the tensile strengths of aluminum and steel are 30,000–40,000 and 80,000–330,000 respectively.

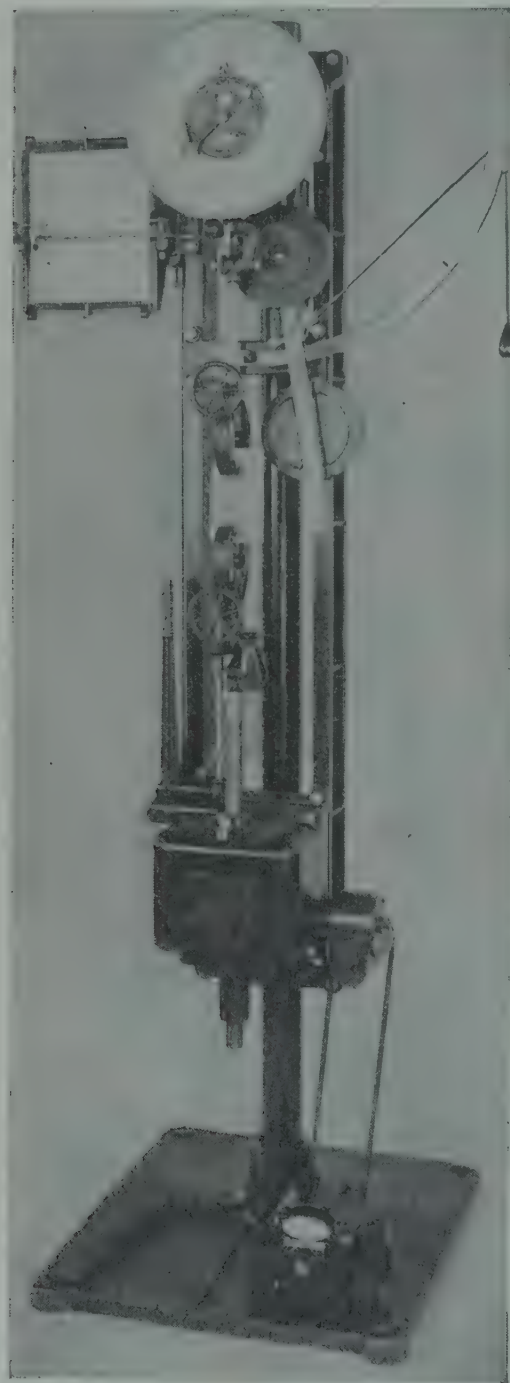


FIG. 5.1. Machine for determining tensile strength. (Courtesy of Henry L. Scott Company.)

The tensile strengths of several plastics are represented graphically in Figure 5.2, in which the range of values are shown by the solid areas. For comparison, the tensile strengths of aluminum and steel are 30,000–40,000 and 80,000–330,000 respectively.

These values indicate the range of strengths which may be produced in the field of high polymers. The actual results obtained depend, however, on many other factors. For example, in compounding a given plastic, the tensile strength may be enhanced by incorporating relatively large amounts of filler with small amounts of plasticizer. In addition, the particular nature of both the filler and the plasticizer will cause a difference. The actual ratio which will finally be used will depend on the other properties desired. As shown in Figure 5.3, an increase in the amount of plasticizer causes an increase in the impact strength and elongation of the plastic, but causes a decrease in the tensile and compressive strengths. The optimum amounts of filler and plasticizer to be incorporated in the plastic for any particular use must be determined experimentally.

Tensile strength values may also be altered by proper physical

processing of the compounded plastic. The method used for molding, or the choice of casting or laminating in preference to molding will result in changes in tensile strength. Comparative results using a

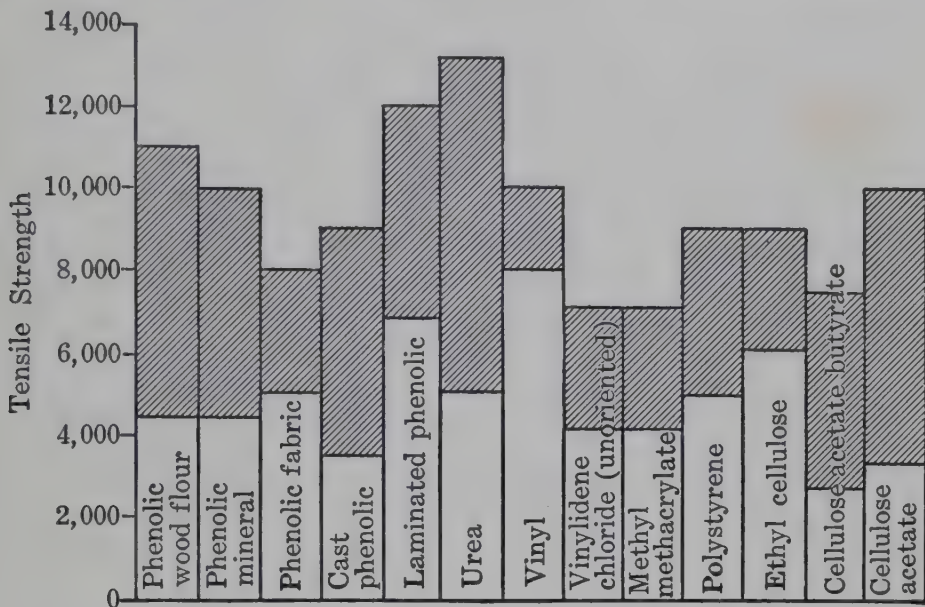


FIG. 5.2. Tensile strengths of common plastics.
(*Product Engineering*, 14(9), 583, 1943.)

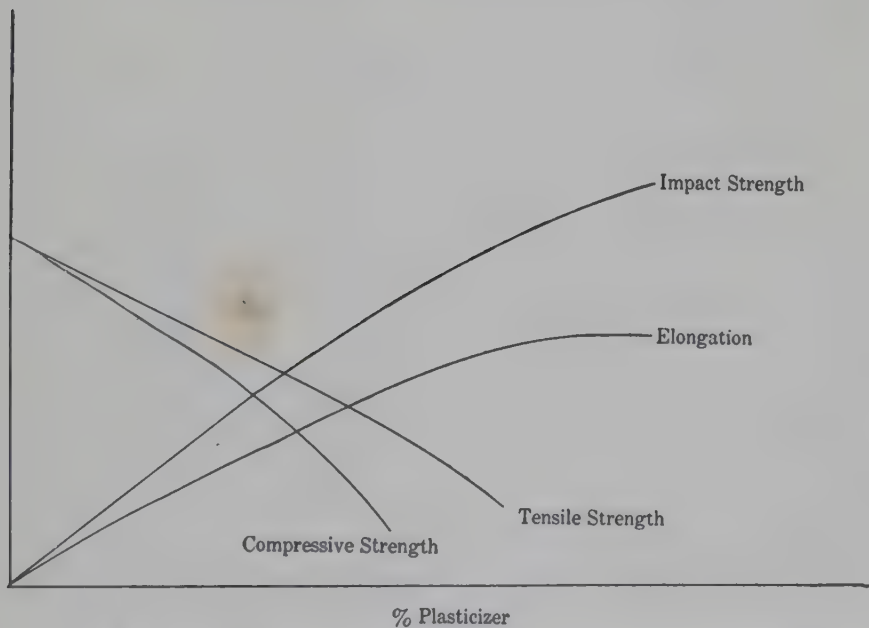


FIG. 5.3. Change of properties with amount of plasticizer.

phenolic resin applied by molding with different fillers, casting, or laminating are illustrated in Figure 5.2. Likewise, physical proces-

sing after fabrication may cause a variation of tensile strength. For example, the strength of extruded fibers of Nylon, Vinyon and rayon may be increased substantially by stretching or "cold-drawing." Polyvinylidene chloride (Saran) may exhibit three ranges of tensile strength depending on the physical state—amorphous, crystalline, or oriented crystalline—in which it is produced. These, in turn, depend upon the processing technique used.

Finally, such chemical considerations as average chain length, degree of branching or cross-linking, and the exact nature of chemical groups present will affect the tensile strength. No general rule may be stated other than that the tensile strength increases with the average molecular weight. In the case of chain polymers the tensile strengths are high because the molecules stretch out by straightening of the kinked or curled macromolecular chain. These molecules may slip past each other slightly. During the stretching operation, also, the influence centers responsible for secondary valence forces become aligned so as to produce the maximum secondary valence effect and thus increase the tensile strength. When a high degree of cross-linking exists in the polymeric structure, the material cannot be stretched to any great extent, yet the tensile strength is generally high. For example, a phenol-formaldehyde resin in which the polymerization has been carried to the thermoset or cross-linked stage, has a high tensile strength but a low elongation.

The testing conditions must be recorded exactly when determining tensile strengths. Variations in temperature have a particularly

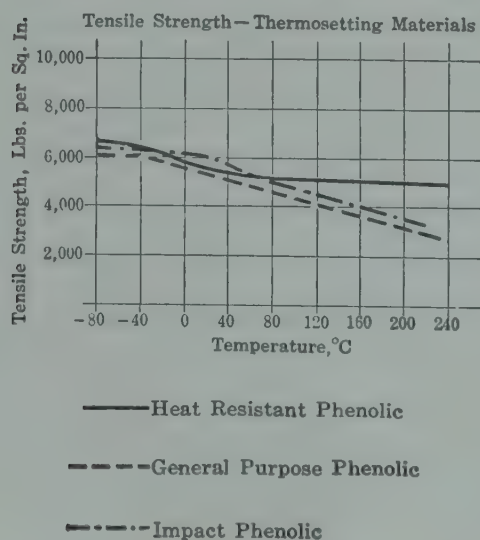


FIG. 5.4. Graph showing effect of temperature on tensile strength. (Courtesy of Monsanto Chemical Co.)

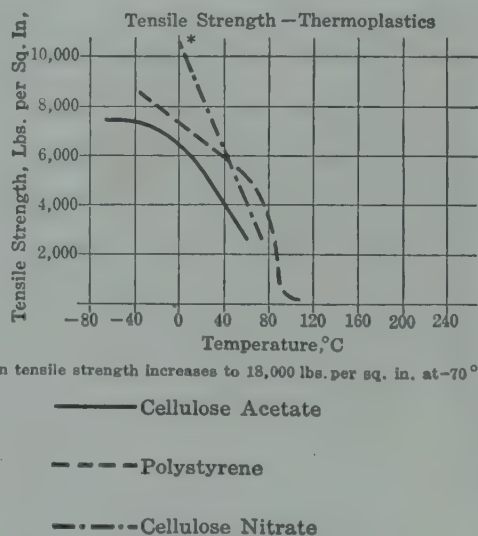


FIG. 5.5. Graph showing effect of temperature on tensile strength. (Courtesy of Monsanto Chemical Co.)

great effect on this property. The tensile strength of both thermosetting and thermoplastic resins decreases as the temperature increases. A comparison of the curves in Figures 5.4 and 5.5 shows that the decrease in tensile strength with increased temperature is much greater with thermoplastic resins than with thermosetting resins.¹

The importance of tensile strength determinations in the plastics industry is emphasized by the number of related properties used to describe plastic performance. The more important of these will be discussed below.

Elastic Hysteresis.—This term is defined more fully in Chapter VIII. The energy absorbed for intermolecular movement when a plastic is stretched and released is expressed by the term, elastic hysteresis.

Tensile Product.—Numerically, this is calculated as the product of tensile strength and elongation at the breaking point.

Compressive Strength.—This factor is closely allied to the tensile strength, but, as the name suggests, it is determined by compression rather than by stretching. It is the compression load at the breaking point divided by the number of square inches of resisting surface. The compression strengths of typical plastics are shown in Figure 5.6. The range of values, in each case, is represented by the solid areas.

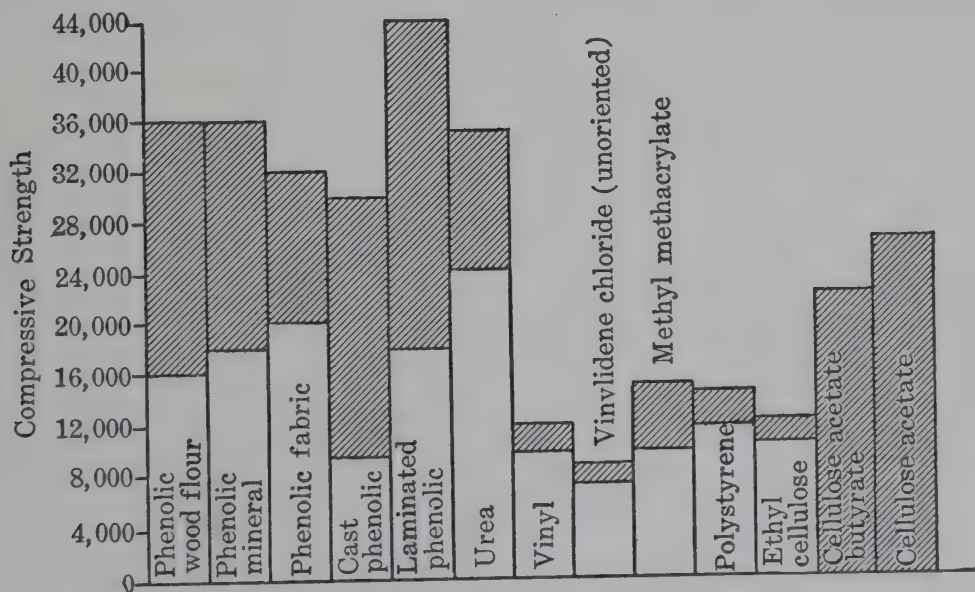


FIG. 5.6. Compressive strengths of common plastics.
(*Product Engineering*, 14 (9), 583, 1943.)

¹ Thermoplastic resins are those which soften when heated. Thermosetting resins harden when sufficient heat is applied and thereafter are infusible.

Elongation.—The increase in length of a measured plastic strip, when stretched to the breaking point, is expressed in terms of the percentage of the original length and is denoted as the elongation. The values of elongation and tensile strength are recorded simultaneously, and are of mutual importance in expressing the behavior of a plastic body.

Tensile strength and elongation are measured by stretching a marked sample at a uniform rate of speed. The elongation is obtained by noting the increase in the distance between two parallel marks on the sample at the breaking point. The tensile strength is simply the force in pounds per square inch required to cause a complete break in the sample. In general, low elongation values are recorded for the cross-linked types whereas the simple linear polymers are capable of greater elongation. This property of the linear polymers is probably due to uninking of the chains with resultant elongation and movement of the chains relative to one another. As in the case of tensile strength, the temperature plays an important role. In this case, however, the values increase as the temperature is raised.

Modulus of Elasticity.—The property of elasticity correlates those of tensile strength and elongation. It may be expressed as the ratio of unit stress to unit strain or as the stress divided by the elongation of a unit length at this stress. The equation representing Hooke's Law may be used to calculate the modulus of elasticity:

$$E = F \frac{L}{\Delta L}$$

where E = modulus of elasticity

F = force applied

L = length of sample

ΔL = increase in length.

The modulus of elasticity is measured only within the range of the elastic limit of the substance concerned. Thus, the values are summarized as values of tensile strengths at various elongations. The particular feature of interest in this property is the indication of rubber-like characteristics or resiliency in plastics. Whereas the values for metals vary from 10,000,000 lbs. per sq. in., to 30,000,000 lbs. per sq. in., those for plastics vary from 60,000 lbs. per sq. in. to 4,000,000 lbs. per sq. in. Since resiliency is the inverse of elastic

modulus, the greater ease of deformation of plastics by stretching is expressed by these values. The data obtained for the modulus of compression do not agree with those for the modulus of elasticity. These differences indicate the importance of the configuration of molecular chains. Straightening of the kinked chains, as discussed above, is a decisive factor in the modulus of elasticity, but is not of the same importance when modulus of compression is determined.

As might be expected, the values for the thermoplastic types (i.e., chain molecules) are lower than those for the cross-linked types. This is easily understood when it is realized that minimum elongations are produced even with high tensile forces in the case of cross-linked polymers. Polymers containing strongly polar groups or possessing a high degree of orientation are more difficult to stretch because of the increased resistance to free movement of the chains provided by the stronger intermolecular forces. These factors are responsible for a higher modulus of elasticity. The moduli of elasticity of several plastics are recorded in Table II-5 together with the values for aluminum and steel.

TABLE II-5. MODULUS OF ELASTICITY ^a

Substance	Lbs. per sq. in. $\times 10^5$
Phenol-Formaldehyde	
Molded	7-45
Cast	5-15
Laminated	4-20
Urea-Formaldehyde	12-15
Polyvinyl Chloride-Acetate Copolymer	3.5-4.1
Polymethyl Methacrylate	6
Polystyrene	1.7-2.6
Cellulose Acetate	0.6-3.5
Cellulose Nitrate	2-4
Ethyl Cellulose	2-4
Aluminum	80-110
Steel	278-290

^a Data on plastics taken from "A Ready Reference for Plastics," p. 54, Boonton Molding Co., Boonton, N. J., 1944.

The values which express the magnitudes of tensile strength and related properties are mainly those which describe the resistance of the plastic to continuous deformation. Other types of deformation are represented in other ways.

Impact Resistance.—Resistance of the plastic to sudden shock or impact is necessary in most applications. Measurements are made by either of the recommended procedures known as the Izod and Charpy methods. These are similar in that they measure the free swing of a pendulum and the swing involved in breaking a test specimen of the plastic. The difference in height to which the pendulum rises (1) when swinging freely and (2) after breaking the

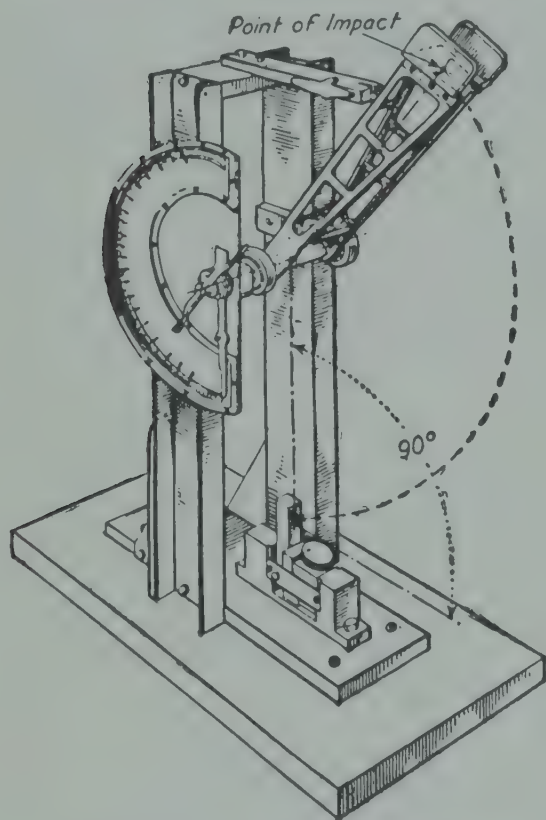


FIG. 5.7. Izod method of determining impact strength. (Simonds and Ellis, *Handbook of Plastics*, p. 67, D. Van Nostrand Co., New York, 1943.)

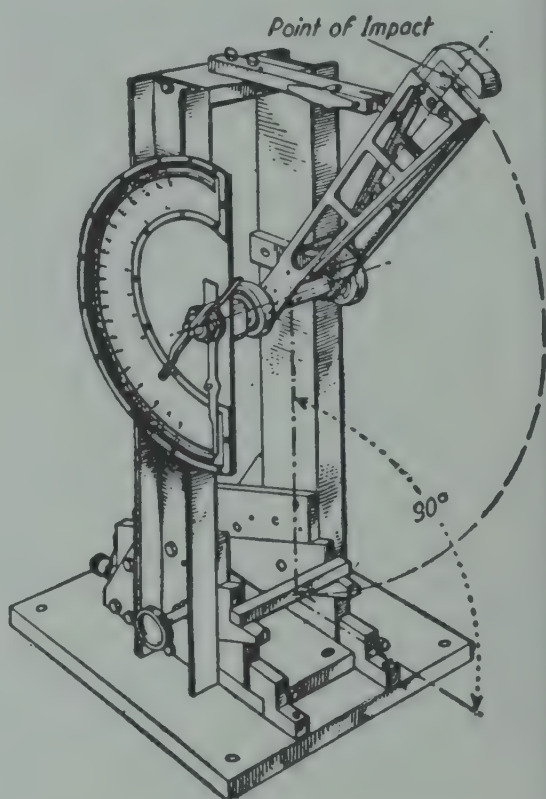


FIG. 5.8. Charpy method of determining impact strength. (Simonds and Ellis, *Handbook of Plastics*, p. 68, D. Van Nostrand Co., New York, 1943.)

test strip is indicative of the energy absorbed in the rupture. The values are then calculated in terms of foot-pounds or centimeter-kilograms. In the Charpy method the notched bar which is to be tested is held horizontally by supports between which the pendulum swings. In the Izod method, the notched bar is held vertically, supported at the bottom.

Range values (solid areas) of impact resistance for several plastics are shown in Figure 5.9.

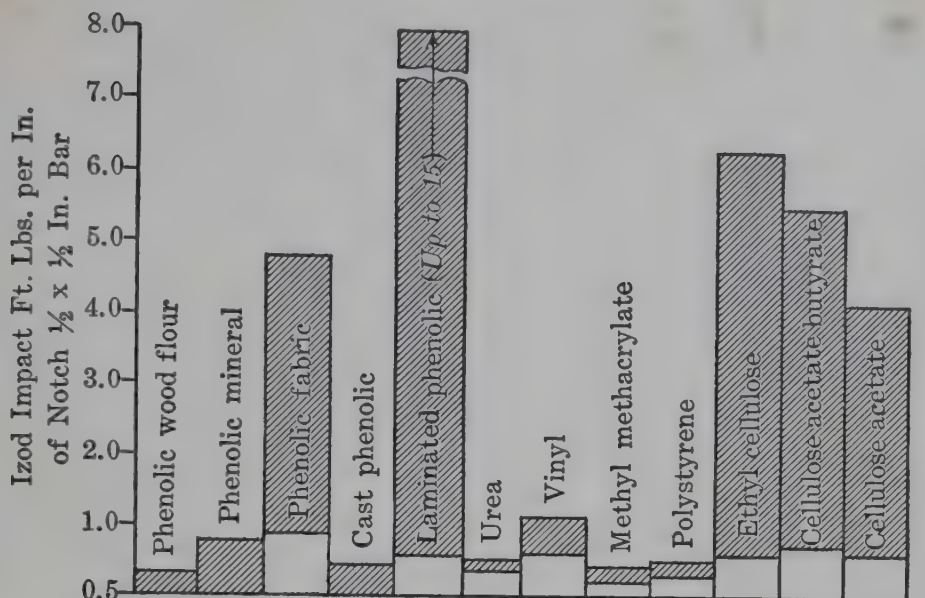


FIG. 5.9. Impact strengths of common plastics.
(*Product Engineering*, 14 (9), 583, 1943.)

Again, the close correlation of physical data with chemical structure is difficult because of the multiplicity of other variants which may alter the values. In general, however, low molecular weight polymers of either straight chain or cross-linked type, are brittle and have poor impact resistance. As the molecular size increases, as in the molding of a phenolic resin, the impact resistance increases. Particular emphasis, however, is placed on the fact that when the degree of cross linkage is excessive, the characteristic of brittleness returns. A direct investigation of such generalizations is difficult because of the fact that proper compounding may markedly increase the resistance of the fabricated plastic to shock. Typical values for a molded phenol-formaldehyde type resin containing various fillers are given in Table III-5. The recorded values again illustrate the unusually great effects contributed by different formu-

TABLE III-5. IMPACT RESISTANCE

Substance	Strength in ft.-lbs./in. of Notch
Phenolic (Wood flour)	0.20-0.40
(Cotton flock)	0.5 -3.0
(Fabric filler)	0.8 -4.8
(Asbestos)	0.5 -2.3
(Mica)	0.2 -0.7

lating ingredients. Then, too, as in the case of tensile strength determinations, the results are materially altered by the conditions of testing and actual service conditions. Figure 5.10 illustrates a comparison of impact resistances at various temperatures and the effect of aging at each temperature. The factor of slow decrease in shock resistance on aging at an elevated temperature is one which is common to most macromolecules.

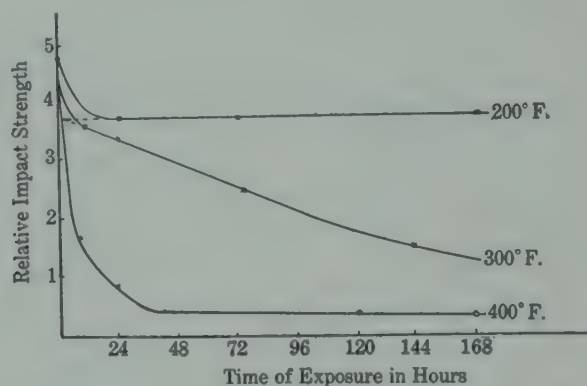


FIG. 5.10. Effect of heat aging upon impact strength. (Del Monte, *Plastics in Engineering*, p. 169, Penton Publishing Co., Cleveland, Ohio, 1942.)

When concerned with rubber-like materials, the factor of impact strength is not of great importance because the values are removed from the critical range. The resiliency of such types is peculiar because of the particular structure responsible for their properties of elasticity and extensibility. The factors inducing such physical characteristics are explained more fully on p. 130.

Flexural Strength.—As the name suggests, the flexural strength expresses the resistance to breaking of the plastic strip as it is bent across its main axis. The property may be measured by a determination of the force necessary to cause rupture of a horizontally-supported bar. Such variables as rate of deflection, bar measurements, deflection produced, and separation of the supports are recorded.

A property which is often correlated with the flexural strength is that which is determined by measurement of the resistance of the plastic to continuous flexing through a known arc. This is known as the fatigue strength. In this case, a bar fixed at one end is bent repeatedly. The number of cycles, force of flexing, arc of deflection, and time involved in the test are critical measurements.

The values of both flexural and fatigue strengths are subject to the same types of chemical considerations and physical variations as

those which have already been discussed. In general, as the impact resistance increases the flexural strength also increases. When physical and testing variations have been carefully excluded, flexural strength will be found to depend on the macromolecular size and relative degree of cross-linking of the polymeric chain. Long linear chains with accompanying free movement of the macromolecules have a high degree of flexibility. Good fatigue resistance and, in most cases, relatively low flexing moduli result. When rigidity is introduced by excessive branching or cross-linkage, higher moduli and decreased susceptibility to continual flexing are encountered.

Hardness and Abrasion Resistance.—Both properties vary according to the ease with which the particles of solid material can be displaced. Scratching, scarring, or wearing by abrasion are all evidences of fine portions of the composite structure being displaced. In practice, the effects of abrasion or poor hardness are expressed in terms of wearing quality, weathering, and permanence of gloss. Prediction of the hardness characteristics is again difficult because of the lack of fundamental chemical concepts. The variables of compounding and service conditions markedly alter the values of these properties.

The general field of amorphous matter may be divided, however, into those materials of particularly poor hardness and those of improved hardness. If hardness is considered as merely resistance to penetration, the resinous bodies of relatively low molecular weight—but having softening points above 70° C.—and substances of the phenol-formaldehyde or urea-formaldehyde type are particularly satisfactory. If, on the other hand, hardness is thought of as resistance to scratching, the same bodies of low molecular weight are considerably poorer than those types of sufficient chain length and resiliency to be classified as elastomers. An increase in the length of the chain and an increase in the amount of cross-linking cause an increase in this type of hardness. Measurements of hardness are obtained by three leading methods:

Shore Hardness. This is an arbitrary value obtained by a gauge measurement of the resistance offered by the plastic surface to penetration of a needle.

Brinell Hardness. This value is obtained by pressing a 2.5 mm. steel ball onto the plastic surface with a measured force and determining the area of the surface of the indentation produced. The Brinell number is calculated by dividing the force applied (expressed in kg.) by the area of indentation (expressed in mm²). The Brinell

TABLE IV-5. HARDNESS ^a

Substance	Brinell Number
Phenol-Formaldehyde	
Molded	30-45
Laminated	24-45
Polyvinyl Chloride-Acetate Copolymer	12-15
Polymethyl Methacrylate	18-20
Polystyrene	20-30
Cellulose Acetate	5-11 (10 kg. load)
Cellulose Nitrate	8-11 (10 kg. load)
Ethylcellulose	4-8.5 (10 kg. load)

^a Data taken from Plastics Properties Chart, opposite p. 48, 1944 ed., *Plastics Catalog*, published by Plastics Catalog Corporation, New York.

hardness numbers of several plastics, as obtained by using a 2.5 mm. ball and a force of 25 kg., are given in Table IV-5.

Rockwell Hardness. These values depend upon the degree of penetration of steel balls, the size of which may vary from 1/16 in. to 1/2 in., when pressed upon the plastic surface.

The abrasion resistance of a linear polymer cannot be compared satisfactorily at elevated temperatures with that of a cross-linked polymer. Since the linear polymers become soft and plastic by the application of heat alone, testing of abrasion will result in erroneous values unless the effect of heat of friction is eliminated. The same consideration applies in a discussion of the machinability of various plastics, since the machining operations involve such steps as turning, swaging, drilling, sawing and polishing. Abrasion resistance, brittleness and the effect of heat play important parts in determining the particular machining operations to be used.

Elastic Properties.—When stress is applied to a plastic body the material may be distorted according to the principles of modulus of elasticity, tensile strength, and elongation. Simultaneously, however, a *plastic* or partially recoverable type of deformation may occur. This type of dimensional change may be caused by even the smallest stresses, but the exact degree depends upon such conditions as magnitude of stress, temperature and rate of application of stress.

Thus, the deformation in a plastics body is composed of two integral types: elastic and plastic. The former is, of course, of much greater magnitude than the latter. It is the main effect up to a certain stress value known as the *elastic limit*. The elastic limit may be variously described as the stress above which Hooke's elastic

behavior law (p. 60) fails to describe the results, or as the value below which the deformation corresponds rather closely to that expected of an elastic (recoverable) body. The typical behavior of a plastic body is represented by the graph of Figure 5.11. The representation

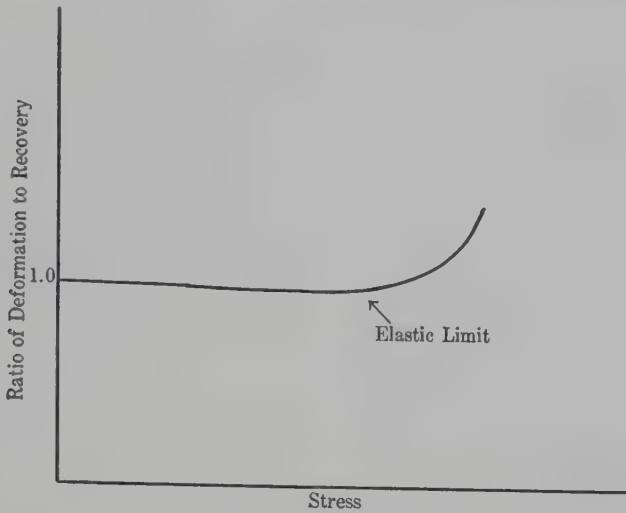


FIG. 5.11. Effect of stress upon deformation/recovery ratio.

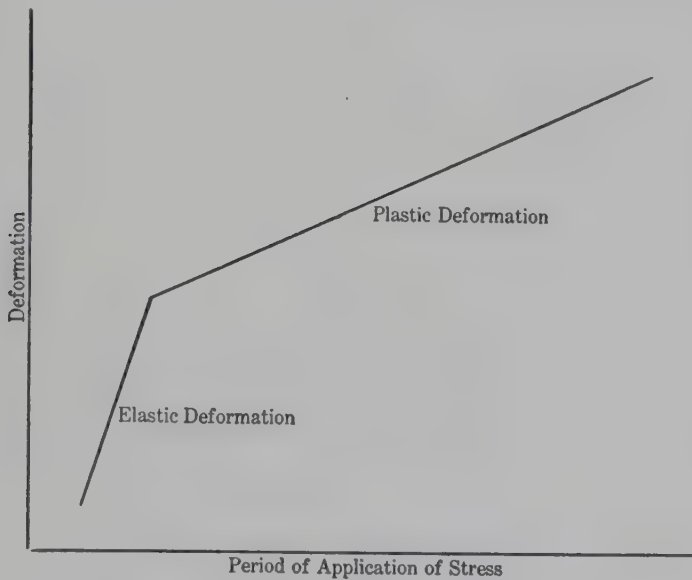


FIG. 5.12. Effect of prolonged stress upon deformation.

does not illustrate the effects produced by varying either the period of stress application or the temperature of testing. The particular effect caused by each factor may be predicted. When small stresses are applied over a long period of time the plastic deformation will become greater than when the same stress is applied for a short

period of time. A typical deformation change with time is represented in Figure 5.12. A temperature increase will, of course, lower the value of the *elastic limit* and will markedly increase the plastic flow.

Certain terms are used to express the types and results of plastic deformation. The distortion under stress may be classified as either *cold flow* or *creep*. The former is reserved to describe a continuous, constant-rate deformation at normal temperatures under small stresses. Creep is also caused by relatively low stresses applied continuously. However, rate of deformation in this case may change with time and extensibility of the plastic.

The result of the distortion involved in plastic deformation is expressed in terms of the amount (expressed in % of original dimension) of distortion which is not recoverable in a specified period of time. This is termed *permanent set*.

The structural considerations involved in a discussion of elastic properties are, fundamentally, a direct comparison of linear and cross-linked structures. In the latter case, deformation of all types is almost negligible below a high value of stress application. The ultimate tensile value is reached without appreciable change in dimensions. When comparing the elastic properties of linear polymers, however, it is found that certain types have a high resiliency or "come-back." These so-called rubber-like or *elastomeric* types possess high elongation values and rapid recovery. Selection of structural characteristics producing such rubber-like products has been the object of prolonged, extensive research. The structural considerations responsible for such behavior are summarized in connection with the discussion of rubber on p. 130. It is sufficient to state here that the macromolecules of highly polar influence centers with their accompanying high secondary valence forces possess low values of creep since the molecules are prevented from slipping over one another. At the opposite extreme, the relatively non-polar polyisobutylene is noted for its cold flow properties.

THERMAL PROPERTIES

In the discussion of mechanical properties, some mention was made of the effects produced by changing the temperature of the plastic body. An increase in the temperature may cause an increase in the plasticity, loss of crystallization regions by thermal agitation of molecular parts, flammability, and decomposition or deterioration of the plastic. These changes are of primary importance in outlining

the performance chart of a given plastic. The basic resins, the plasticizers and some of the fillers used in fabricating a plastic article are organic compounds. Like the simpler organic compounds, plastics may be changed chemically by heat. Furthermore, variations in heat conductance and heat absorption are important factors in the commercial utilization of certain plastics. The more important thermal properties to be discussed are:

1. Thermal conductivity.
2. Specific heat.
3. Heat distortion point.
4. Continuous heat resistance.
5. Flammability.
6. Coefficient of thermal expansion.

Thermal Conductivity.—This property may be defined as the time rate of transfer of heat through unit thickness and area when between temperatures of unit gradation. A diagrammatic sketch of the testing procedure is shown in Figure 5.13. By reference of the unknown to a standard the measurements may be determined when the temperature gradients at equilibrium are known. Calculation

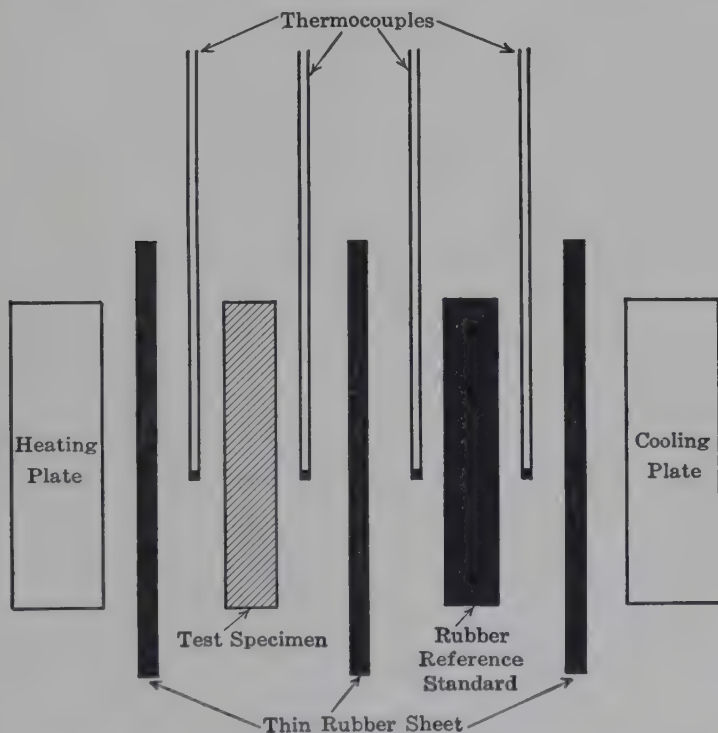


FIG. 5.13. Testing of thermal conductivities. (Simonds and Ellis, *Handbook of Plastics*, p. 96, D. Van Nostrand Co., New York, 1943.)

of the desired value may then be made:

$$k = k_r \frac{D}{D_r} \times \frac{t_r}{t}$$

- where k = thermal conductivity of unknown
- k_r = thermal conductivity of reference material
- D = thickness of unknown specimen
- D_r = thickness of reference specimen
- t = temperature gradient across test specimen
- t_r = temperature gradient across reference specimen.

As a general rule the values obtained in measuring this property of plastics indicate a low conductance. Low values cause plastics to be very desirable in certain applications, such as handles for flatirons and coffee pots. In others, low heat conductance renders the plastic bodies unfit for service. When heat must be conducted rapidly, specially formulated types of plastics must be prepared, or these materials must be replaced by metals. Non-metallic bearings, for example, have proved valueless for certain applications because of their poor thermal conductivity.

HEAT CONDUCTION
(Thermal Conductivity) (Poorest to Best)

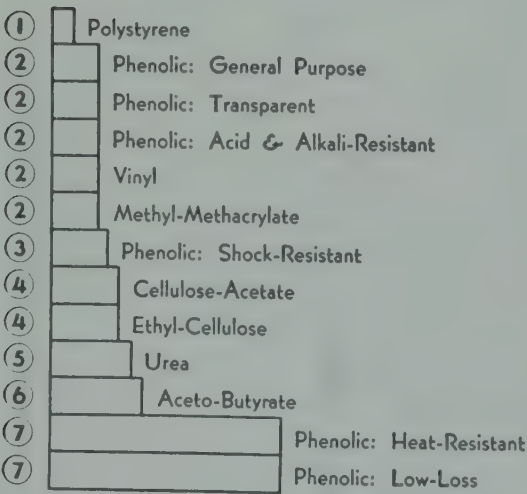


FIG. 5.14. (Plastics Comparator, (Copyrighted by Bakelite Corporation.)

of a few common materials. A graphical representation of heat conductivities is shown in Figure 5.14.

Low thermal conduction is also particularly unfavorable in the processing of various plastics. Certain chemical and physical changes are brought about in mechanical applications by subjecting the plastic material to heat and pressure, as in the processes of molding and laminating. When heat conduction is poor, difficulty in obtaining a uniform product may be encountered. A knowledge of the thermal characteristics of a plastic is absolutely essential for an accurate prediction of the best processing procedure. Some relative values are recorded in Table V-5, together with the thermal conductivities

TABLE V-5. THERMAL CONDUCTIVITY ^a

Substance	$\times 10^{-4}$ cal./sec./sq. cm./1° C./cm.
Phenol-Formaldehyde	
Molded	2-20
Cast	3-8.4
Laminated	5-8
Urea-Formaldehyde	7.1
Polyvinyl Chloride-Acetate Copolymer	3.9-4.0
Polymethyl Methacrylate	4-6
Polystyrene	1.9
Nylon, Molded	6
Cellulose Acetate	4.5-7.8
Cellulose Nitrate	3.1-5.1
Ethyl Cellulose	3.8-6.3
Felted Cotton	0.33
Asbestos Fiber	1.9
Cork	7.2
Aluminum	5000.

^a Data on plastics taken from Plastics Properties Chart, opposite p. 48, 1944 ed., *Plastics Catalog*, published by Plastics Catalog Corporation, New York.

Specific Heat.—The specific heat of a substance is the amount of heat necessary to raise the temperature of one gram of the substance

TABLE VI-5. SPECIFIC HEATS ^a

Substance	Cal./gm./°C.
Phenol-Formaldehyde	
Molded	0.25-0.4
Cast	0.3 -0.4
Laminated	0.3 -0.4
Urea-Formaldehyde	0.4
Polyvinyl Chloride-Acetate Copolymer	0.24-0.5
Polymethyl Methacrylate	0.35
Polystyrene	0.32
Nylon, Molded	0.55
Cellulose Acetate	0.3 -0.42
Cellulose Nitrate	0.34-0.38
Ethyl Cellulose	0.32-0.46
Aluminum	0.214
Steel	0.107
Copper	0.092
Lead	0.0306

^a Data on plastics taken from Plastics Properties Chart, opposite p. 48, 1944 ed., *Plastics Catalog*, published by Plastics Catalog Corporation, New York.

one degree Centigrade. The data in Table VI-5 show that the specific heats of typical plastics are appreciably higher than those of metals. It is obvious that the lower the specific heat of a plastic, the lower the heating costs when it is subjected to a molding process.

Heat Distortion Point.—The behavior of plastic bodies in relation to this characteristic of heat distortion is the fundamental basis used for the division of these materials into two groups: *thermoplastic* and *thermosetting*. As the names imply, the former always exhibits the property of softening with heat while the latter hardens or cures when heat is applied. After curing has taken place, the material will no longer soften or flow when heated. During the hardening process of a thermosetting resin, the heat causes certain chemical changes which result in the formation of a compact, cross-linked, interdependent system. The lack of free functional groups in the thermoplastic linear polymer prohibits further chemical action when heat is applied and this type, therefore, remains permanently plastic on heating. The structural considerations responsible for the formation of both types have been discussed on pages 37-41. In a practical application the hardening of a thermosetting resin is carried out during the final processing. The chemical reaction by which it is prepared, therefore, is not completed until such a process as molding or laminating is carried out. In this final step it is necessary to have an excess of one of the reactants or some other suitable compound in order to bring about cross-linking.

TABLE VII-5. HEAT DISTORTION TEMPERATURES ^a

Substance	°F.
Phenol-Formaldehyde	
Molded	240-320
Cast	113-176
Laminated	> 320
Urea-Formaldehyde	260-280
Melamine-Formaldehyde	266-385
Polyvinyl Chloride-Acetate Copolymer	140-150
Polymethyl Methacrylate	125-165
Polystyrene	170-175
Nylon, Molded	149
Cellulose Acetate	100-215
Cellulose Nitrate	120-165
Ethyl Cellulose	120-200

^a Data taken from Plastics Properties Chart, opposite p. 48, 1944 ed., *Plastics Catalog*, published by Plastics Catalog Corporation, New York.

The effect of heat upon the usefulness of a plastic body depends, therefore, principally on the type of plastic used. In the case of thermoplastics, a definite temperature (i.e., softening point) may be used to represent the highest practical service temperature even when no stress is involved. The maximum serviceable temperature under stress is represented by the values of heat distortion point under the influence of some loading. The lowest temperature at which the material being tested (a 1/2 in. X 1/2 in. X 5 in. molded bar), yields a specified distance (0.01 in.) with a loading of 5.5 lbs., is defined as the distortion point of the plastic. Generally, relatively low values, 60–95° C. (140–200° F.), are encountered when thermoplastics are tested, while higher values are found in the case of thermosetting materials. (See Table VII–5.)

Continuous Heat Resistance.—Of more importance in predicting the serviceability of thermosetting types of materials is the value of *continuous heat resistance*. The value used is the maximum temperature at which the sample does not change its form (not over 1% change in length) or color. This value is the best criterion available to determine how well the finished plastic will withstand elevated temperatures under actual operating conditions. Although thermosetting resins do not soften with heat to any extent, excessive or prolonged heat treatment may result in excessive hardening, contraction, charring, or disintegration. Even at relatively low temperatures the urea-formaldehyde resins tend to become brittle on prolonged aging. Probably such effects as contraction and em-

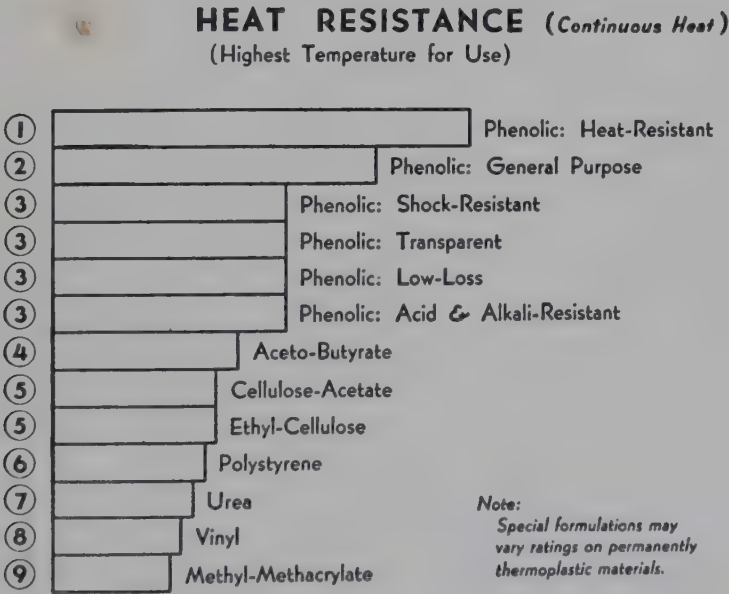


FIG. 5.15. (Plastics Comparator, Copyrighted by Bakelite Corporation.)

brittleness are caused by a continuation of the chemical reaction by which the material hardens. The continuous heat resistance values of several resins are represented graphically in Figure 5.15.

Flammability.—Certain plastics, e.g., nitrocellulose, show notoriously great flammability while others such as the phenolics burn only with great difficulty or not at all. From structural considerations the compact thermosetting types may be expected to be in the latter category. The linear polymers differ from one another according to the nature and arrangement of the atoms present. Those plastics, for example, which contain a high proportion of chlorine in the molecule show reduced flammability. Figure 5.16 shows some typical plastics arranged in the order of increasing flammability.

FLAMMABILITY

Inverse ratio of the time piece continues to burn after removal from gas flame

- ① { Phenolic: Heat-Resistant
Phenolic: Low-Loss
- ② { Phenolic: Acid & Alkali-Resistant
Phenolic: Transparent
- ③ Phenolic: General Purpose
- ④ Phenolic: Shock-Resistant
- ⑤ Urea, Vinyl
- ⑥ { Polystyrene
Aceto-Butyrate
Cellulose-Acetate
Ethyl-Cellulose
Methyl-Methacrylate

FIG. 5.16. (Plastics Comparator, Copyrighted by Bakelite Corporation.)

Coefficient of Thermal Expansion.—The dimensional changes caused by an elevation of temperature are expressed in terms of the coefficient of expansion. This value represents the change in unit dimension caused by a temperature rise of one degree Centigrade. These data are of great importance in fabrication and processing. For example, when plastics are used in combination with other materials, such as metals, the difference between the expansion tendencies of each necessitates certain precautions or changes. Differences in expansion may cause loose-fitting parts unless corrected for in the manufacture or design.

Then, too, the elevated temperatures of such processes as molding or casting indicate that the fabricated article will shrink as it is cooled to room temperature. Knowledge of the exact dimensional change which may result from this temperature change is essential before proper design of the mold cavity can be completed. In such a case, a correlation of the expansion which may occur in both the mold and plastic article must be carefully made.

ELECTRICAL PROPERTIES

Although plastics, in general, have been found to possess excellent insulation characteristics, considerable care must be used in making and compounding a plastic for use as an insulator. For example, it is imperative to exclude all moisture from the plastic. As a rule, those plastics which have the greatest resistance to moisture also show a high degree of usefulness as insulators. Furthermore, a careful selection of compounding agents—fillers, plasticizers, lubricants—is necessary, for these added compounds detract from the optimum electrical properties which can be obtained with the resin alone.

The following electrical properties will be discussed:

1. Dielectric constant.
2. Dielectric strength.
3. Power factor.
4. Insulation resistance.
5. Arc resistance.

Dielectric Constant.—The values of dielectric constant represent the effectiveness of a material as an insulating medium when it is placed between two charged plates in a condenser. The dielectric constant may be expressed as the ratio of the effectiveness of the sample to that of air. The values show a marked variation with variation in electrical frequency. As far as correlation with chemical structure is concerned, it is found that materials of polar nature are decidedly poorer insulating media than those substances of non-polar character. Two plastics with high dielectric constants are polystyrene and polyethylene. These materials are comparable to fused quartz in effectiveness, so far as most electrical properties are concerned.

Dielectric Strength.—Values of this property represent the specific resistance of each plastic to high voltages. Some plastics show excellent results while others can be improved by the addition of a suitable filler such as mica. In actual determinations, three methods may be used in expressing the dielectric strength of an unknown.

These may be spoken of as the *instantaneous*, *step-by-step*, and *endurance* dielectric strengths. As the names suggest, the first is determined by increasing the voltage at a slow uniform rate until breakdown occurs; the second, by the application of a step-wise increase in voltage; and the last represents the continual resistance of the plastic when subjected to high voltage for a considerable period of time. The comparative instantaneous dielectric strengths of several plastics are represented in Figure 5.17.

DIELECTRIC STRENGTH

(A.S.T.M. $\frac{1}{8}$ " Instantaneous)

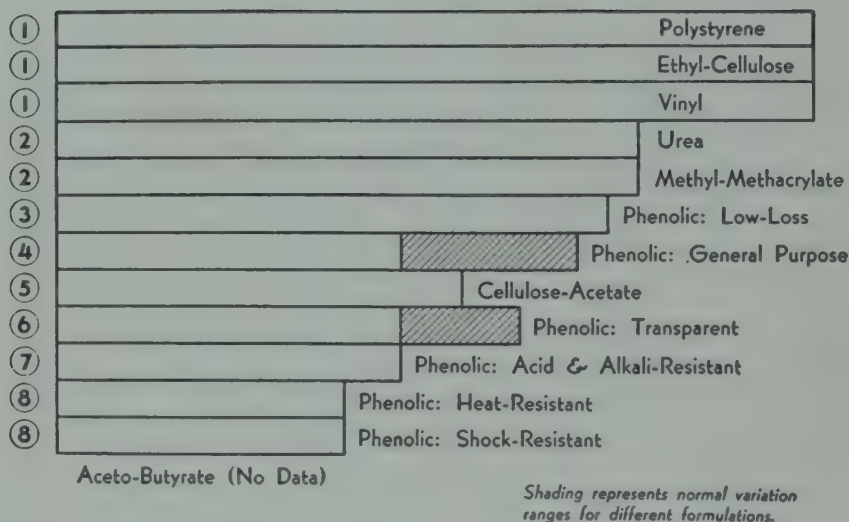


FIG. 5.17. (Plastics Comparator, Copyrighted by Bakelite Corporation.)

Power Factor.—The measure of power absorbed by an insulating material in the presence of an alternating current field is known as the power factor. With a perfect insulator, there would be no power loss, i.e., no power would be absorbed by the insulating material. Polystyrene, polyethylene, and quartz approach the zero value closely, but variations in temperature, moisture content, cold flow, and compounding agents may cause higher values. This property is of particular importance when seeking to apply plastics to radio or communication work. Table VIII-5 gives the power factors at different frequencies of several plastics.

Resistivity.—In addition to the other electrical characteristics of plastics, they are particularly valuable because of their resistance to the passage of an electric current. The volume resistivity is determined by measurement of the reciprocal of the current which will

TABLE VIII-5. POWER FACTORS ^a

Substance	60 cycles per sec.	1000 cycles per sec.	1,000,000 cycles per sec.
Phenol-Formaldehyde			
Molded	0.01 -0.3	0.01 -0.2	0.005 -0.5
Cast	0.10 -0.15	0.01 -0.05	0.02 -0.05
Laminated	0.05	—	0.01 -0.08
Urea-Formaldehyde	0.04 -0.055	—	0.027 -0.035
Polyvinyl Chloride-Acetate			
Copolymer	0.008 -0.084	0.01 -0.123	0.014 -0.100
Polymethyl Methacrylate	0.05 -0.07	0.04 -0.07	0.02 -0.03
Polystyrene	0.0001-0.0003	0.0001-0.0003	0.0001-0.0008
Nylon, Molded	0.018	0.050	—
Cellulose Acetate	0.01 -0.07	0.01 -0.06	0.01 -0.09
Cellulose Nitrate	0.06 -0.15	—	0.07 -0.10
Ethyl Cellulose	0.005 -0.015	0.005 -0.025	0.007 -0.030

^a Data taken from Plastics Properties Chart, opposite p. 48, 1944 ed., *Plastics Catalog*, published by Plastics Catalog Corporation, New York.

pass between electrodes covering opposite faces of a unit centimeter cube of the material when unit potential gradient exists between the electrodes. The resistivity of a good insulator should be in the

TABLE IX-5 ^a**RESISTIVITY**

(Rating from Highest to Lowest) Lowest is expressed as unit (1)

(All are Good Insulators for Direct Current)

* ① Polystyrene	10 ⁸
* ② Ethyl-Cellulose	10 ⁵
* ③ Vinyl	10 ⁴
③ Phenolic: Low-Loss	10 ⁴
④ Urea	2000
⑤ Phenolic: Transparent	120
⑥ Cellulose-Acetate	100
⑦ Phenolic: General Purpose	13
⑧ Phenolic: Heat-Resistant	2
⑨ Phenolic: Shock-Resistant	1

No data Aceto-Butyrate & Phenolic: Acid & Alkali Resistant

* Considering high resistivity of poorest is excellent, figures are fantastic for higher ones.

^a Plastics Comparator, Copyrighted by Bakelite Corporation.

Resistivity Spectrum

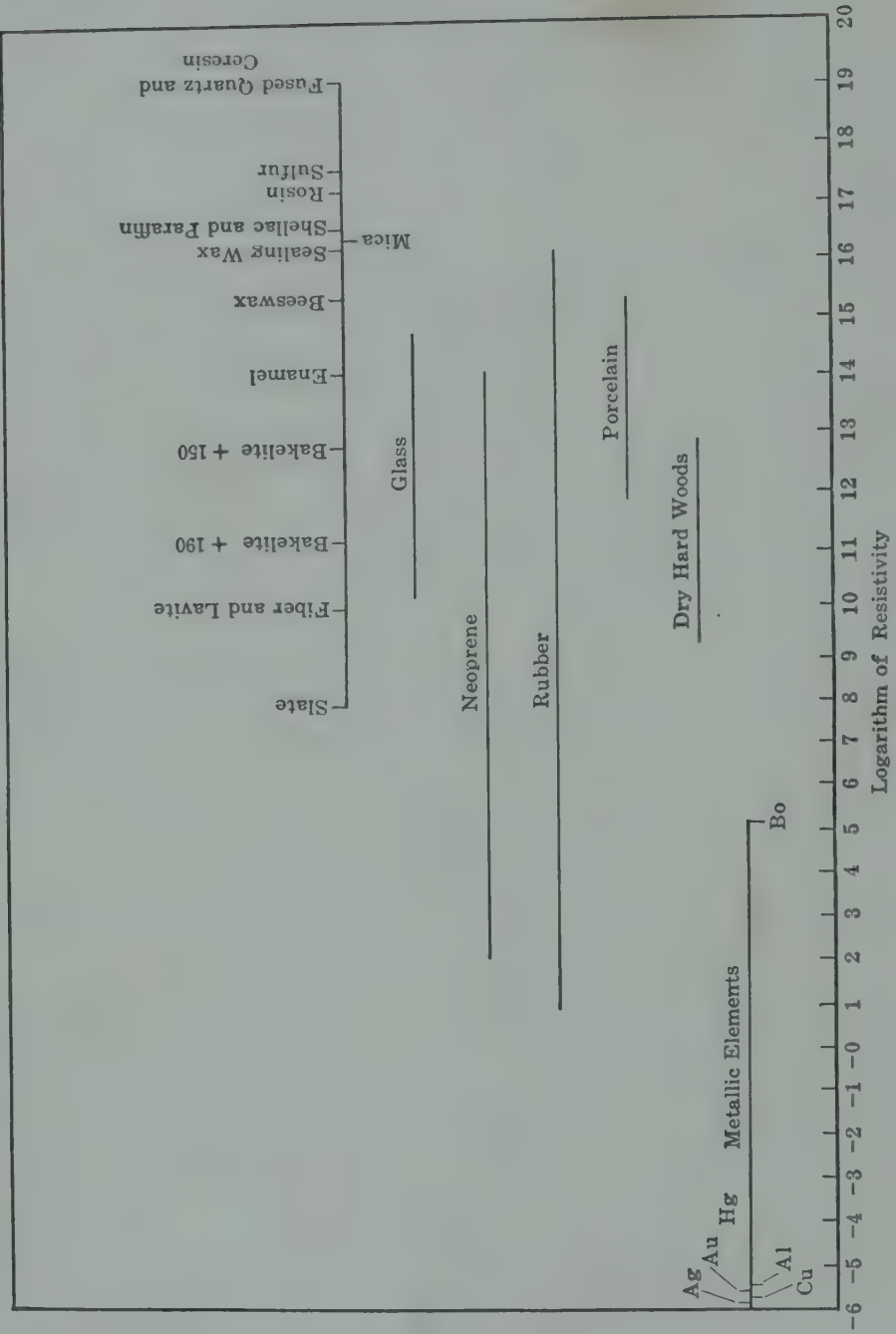


FIG. 5.18. Resistivity spectrum. (Yerzley, *Ind. Eng. Chem.* 35, 330, 1943.)

vicinity of 10^{16} ohms/cm. At the opposite extreme a metal conductor is recorded as having a resistivity of 10^{-6} ohms/cm. The resistivity of polystyrene is 10^{18} ohms/cm. All of the plastics are characterized by high resistivity. A resistivity spectrum, including values recorded for rubber and neoprene compounds, has been depicted by Yerzley. It is represented in Figure 5.18, and the comparative resistivities of several plastics are represented in Table IX-5.

Arc Resistance.—This term refers to the resistance of a plastic strip to the passage of an electric arc. In most cases the tendency of the organic plastics is to decompose with the formation of carbon tracks. Thus, most plastics have poor arc resistance. Under general conditions, the products formed from acrylic esters or urea and formaldehyde are the most desirable of the synthetic plastics. Cold-molded asphaltic substances also offer maximum arc resistance.

OPTICAL PROPERTIES

Colorability.—Many applications of plastics require favorable optical characteristics. The most important characteristic is colorability. Since many plastics are used in the manufacture of artistic objects and since it is desirable to have any product look as attractive as possible, the problem of obtaining beautifully colored plastics has received considerable attention. Although most plastics can be obtained in a wide variety of colors, it should be noted that molded phenolic resins are available in only a few colors. Colors may be introduced in plastics by means of organic dyes or inorganic pigments.

Index of Refraction.—This property, so familiar to the study of optical characteristics, is defined as the ratio of the velocity of light in a vacuum to its velocity in the material being tested. Since direct measurement of the velocity of light in the material is experimentally difficult, the index of refraction is usually measured as the ratio of the sine of the angle of incidence to the sine of the angle of refraction, i.e.,

$$n = \frac{\sin i}{\sin r}$$

The path of the beam of light and the angles of incidence and refraction are illustrated in Figure 5.19. The index of refraction is of value for the identification of certain plastics, for the construction of plastic lenses, and for the determination of the reflection of light by plastics.

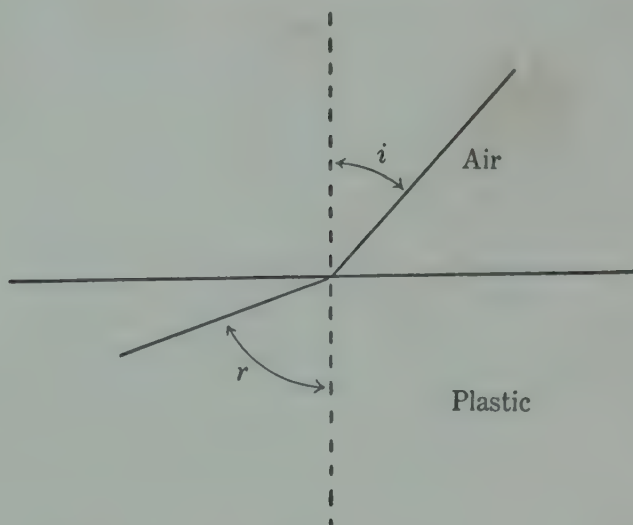


FIG. 5.19. Bending of a light beam as it passes through different media.

Light Transmission.—The transparency of plastics is measured by determining the fraction of incident light which is transmitted by the plastic. The value is expressed as the percentage of incident light transmitted by the plastic as measured by a photoelectric cell. Such plastics as polymethyl methacrylate and polystyrene exhibit particularly high values (92% and 90%).

Light Diffusion.—When plastics cause diffusion of the incident light, they are suitable for a variety of uses in the lighting and decorative industries. Determinations are made by measurement of diffused light by a photoelectric cell held at various angles to the surface of the sample being tested. Diffused light of both reflected and transmitted nature may be determined.

CHEMICAL PROPERTIES

Solubility.—The properties of molecular weight values and solubilities of polymeric molecules are so closely related that one cannot be discussed without direct reference to the other. Three fundamental generalizations concerning the solubilities of polymers may be summarized as follows:

1. The most general solubility rule in the field of organic chemistry, namely that a solute is most soluble in a solvent of similar chemical structure, also holds in the case of polymers.

2. Molecules of high molecular weight are less soluble and produce solutions having higher viscosities than analogous polymers of low molecular weight.

3. The solubility of polymeric chains decreases as the amount of branching increases and becomes negligible with the introduction of cross-linkages.

The first of these solubility generalizations may be expressed by the simple phrase, like dissolves like. For example, polyvinyl alcohol $(-\text{CH}_2\text{CHOH}-)_x$ has a high proportion of hydroxyl groups and hence is soluble in water and the low molecular weight alcohols. Polyvinyl alcohol is insoluble in hydrocarbon solvents; in fact a flexible tubing has been made from polyvinyl alcohol for use in transporting such hydrocarbons as gasoline, kerosene, and fuel oil. On the other hand, polystyrene, $(-\text{CHCH}_2-)_x$ is a hydrocarbon



molecule, and is insoluble in such solvents as water and alcohol. It is soluble, however, in hydrocarbon solvents such as benzene and toluene. An examination of the formula for polystyrene shows that it contains a higher proportion of aromatic hydrocarbon than of aliphatic hydrocarbon. Consequently, one would predict that it would be more soluble in aromatic hydrocarbon solvents than in aliphatic hydrocarbon solvents. This prediction is in agreement with the experimentally determined solubilities. One other illustration of this generalization is the fact that the polyalkylacrylates, which contain a high proportion of ester groups, are soluble in simple esters such as ethyl acetate and, like most other esters, are insoluble in water. It should be mentioned that this rule is also of great importance in selecting the proper type of plasticizer for use with a given polymer, for in this case, also, mutual solubility is desired.

TABLE X-5. POLYSTYRENE POLYMERS ^a

Material	Formula	Mol. Wt.	Solubility in Ether	Melting Point ° C.
Dimer	$\text{C}_{16}\text{H}_{16}$	208	Sol.	liquid
Trimer	$\text{C}_{24}\text{H}_{24}$	312	Sol.	liquid
SnCl_4 polymerization	$\text{C}_{240}\text{H}_{240}$	3,000	Sol.	105-110
Polymerized in N_2 at 150° C.	$\text{C}_{1,840}\text{H}_{1,840}$	23,000	Insol.	120-130
Polymerized in N_2 at 100° C.	$\text{C}_{9,600}\text{H}_{9,600}$	120,000	Insol.	160-180
Polymerized in air at 20° C.	$\text{C}_{16,600}\text{H}_{16,600}$	200,000	Insol.	180
A fraction from room temperature polymerization in N_2	$\text{C}_{48,000}\text{H}_{48,000}$	600,000	Insol.	180


^a Staudinger, *Die Hochmolekularen Organischen Verbindungen*, Van J. Springer, p. 186, Berlin, 1932.

The relationship of solubility to molecular weight is in line with the facts which have been observed in the study of simpler organic compounds. As the molecular weight increases, the solubility decreases and the resistance to solvation increases. The relationship between the solubilities and molecular weights of some styrene polymers is shown in Table X-5.

Furthermore, as the particle size increases, the interference of each particle with its neighbors increases, resulting in an increase in viscosity. A series of standard solutions of polymers of differing molecular weights, but obtained from the same monomer, show a rapid bodying (increase in viscosity) as the particle size increases.

This relationship between viscosity and molecular weight is the basis of Staudinger's method² of determining the molecular weights (particle size) of macromolecules. The viscosity of a standard solution is often used in the marketing of a commercial resin in order to represent the different types available. For example, several different polymers of vinyl acetate are available commercially. They are represented as having viscosities of $1\frac{1}{2}$, $2\frac{1}{2}$, 7, 15, 25, 45, or 60 centipoises³ in a standard solution.

The third generalization concerning the solubility of polymers is that the solubility decreases with increasing branching and that cross-linked polymers are insoluble. It has already been pointed out (p. 41) that branching may be so extensive that the branched polymer may closely resemble a cross-linked polymer in its properties.

An interesting example of the effect of cross-linking on solubility is found in the polymerization of commercial styrene. The presence of traces of divinylbenzene $\text{CH}_2=\text{CH}$  $\text{CH}=\text{CH}_2$ as an impurity in commercial styrene was found to be the cause of the formation of an insoluble polymer. When the divinylbenzene was removed and the styrene polymerized under identical conditions, a soluble polymer was obtained. The formula for divinylbenzene shows at a glance the possibility of establishing cross-linkages. It is interesting to note that even though the polymers obtained with

² Staudinger, *Die Hochmolekularen Organischen Verbindungen*, pp. 52-72 (1932), Van J. Springer, Berlin.

³ A poise is the viscosity of a hypothetical liquid such that a force of one dyne per square centimeter causes two parallel liquid surfaces one square centimeter in area and one centimeter apart to slide past one another with a velocity of one centimeter per second.^a A centipoise is 0.01 poise.

^a Getman and Daniels, *Outlines of Theoretical Chemistry*, 7th ed., p. 167, John Wiley & Sons, Inc., New York.

divinylbenzene present were insoluble, they did swell when placed in a suitable solvent. It was found that the amount of swelling produced was inversely proportional to the amount of divinylbenzene present. These facts suggest the possibility that the solubility of a linear polymer is due to the separation of a bundle or micelle of chains into the single component chains. The solvent is pictured as reducing the attractive forces (secondary valences) existing between neighboring chains. However, when the binding force between these chains consists of actual primary valence linkages, separation is impossible, the polymer is insoluble, and the degree of solvation (swelling) is dependent upon the amount of cross-linking present. Furthermore, the ease of solubility of a linear polymer may be pictured as being dependent, in some measure at least, on the actual amount of attraction created by the secondary valence forces holding the molecular bundles together. As these secondary valence forces increase, the ease with which the solvent separates the molecular chains decreases. The solubilities of polyvinyl chloride ($-\text{CH}_2\text{CHCl}-$)_x and polyvinylidene dichloride ($-\text{CH}_2\text{CCl}_2-$)_x in all solvents are low. It is believed that strong secondary valence forces exist in these polymers. These polymers do swell appreciably, however, indicating that the solvent, by association with the polymeric material (solvation), is capable of causing swelling to the gelatinous condition.

A solubility effect which has been mentioned briefly on page 21 is that of thixotropy. The term is applied to a particular type of solution which exists in the conditions of both a free-flowing liquid and a swollen, gelatinous mass. When the solution is freshly prepared or subjected to rapid agitation, the viscosity is decreased to a value consistent with free flow. When, however, the solution is allowed to remain at rest, the viscosity will increase and, under most conditions, a gel structure will result. Upon reagitation, the free-flowing condition is again produced.

The phenomenon of thixotropy as exhibited by clays and other inorganic colloidal particles in aqueous suspension appears to depend upon the concentration of electrolytes present.⁴ However, electrolytes are not present in solutions of copolymers of vinyl chloride and vinyl acetate in organic solvents such as ketones, nitromethane, and chlorinated hydrocarbons, and yet these solutions exhibit the phenomenon of thixotropy at certain concentrations. In such a case, it seems necessary to assume the existence of strong secondary valence forces exerted between molecules and acting across the

⁴ (a) Hauser, *Colloidal Phenomena*, p. 216, 1st ed., McGraw-Hill Book Co., N. Y., 1939; (b) Ostwald, *J. Phys. Chem.* **42**, 981 (1938).

liquid solvent boundary. When the solution is allowed to stand undisturbed, these attractive forces exert a maximum effect and cause the formation of a gel structure, accompanied by the cessation of the Brownian movement of the particles. These secondary valence forces of attraction, however, can be overcome by mechanical stirring to form a mobile liquid, with the resumption of the Brownian movement of the colloidal particles.

Compatibility.—The physical property of compatibility is also one which may be correlated directly with the generalizations concerning solubility which have just been discussed. The ability of a high molecular weight polymer to be mixed with other plastics or compounding agents (plasticizers, lubricants, gums, waxes, asphalts) depends, in a general way, on the three factors mentioned in connection with solubility. They may be summarized as follows:

1. Compatibility increases when similarity of structure or polarity exists.
2. Compatibility decreases with increasing molecular weight.
3. Compatibility decreases with increasing degree of branching or cross-linking.

Resistance to Acids, Alkalies, and Ozone.—The characteristic of resistance to chemicals is of the utmost importance in many applications of plastics. Search for a theoretical basis upon which predictions of behavior in any unknown case might be founded have not been particularly fruitful. Certain generalizations may be mentioned, however, as some guidance for such a prediction.

First, the presence of any group in the resin or plastic which may be readily attacked will, of course, materially reduce the resistance in that particular case. For example, the phenol-formaldehyde resins all contain phenolic groups. Since phenols are soluble in alkali, it is not surprising that these resins have a poor resistance to a strong alkali. The resistance to alkali is even further decreased by the introduction of a second hydroxyl group as in the resorcinol-formaldehyde resins. Polyacrylic acid is, of course, readily attacked by alkali because of the presence of many carboxyl groups in the molecule. Polystyrene, the vinyl copolymers, and polyethylene appear to have the greatest resistance toward acids, alkalies, and water as shown in Tables XI-5, XII-5, and Figure 5.20.

It is a well-known fact that a molecule which contains several unsaturated linkages is susceptible to oxidation. Rubber, which is considered as a polyisoprene, has a considerable number of double bonds per molecule and hence is easily destroyed by the action of

TABLE XI-5^a**ACID RESISTANCE**

(From Best to Worst)

	<u>WEAK</u>	<u>STRONG</u>
① { Polystyrene Vinyl	Excellent "	Excellent "
② { Phenolic: Acid & Alkali-Resistant Methyl-Methacrylate	Very Good "	Good to other than Strong Oxidizing
③ { Phenolic: Transparent Phenolic: General Purpose	Fair "	"
④ {	Phenolic: Heat-Resistant	"
	Phenolic: Shock-Resistant	Poor "
	Urea	"
	Cellulose-Acetate	"
	Ethyl-Cellulose	"
	Aceto-Butyrate	"

^a Plastics Comparator, Copyrighted by Bakelite Corporation.TABLE XII-5^a**CAUSTIC RESISTANCE**

(From Best to Worst)

	<u>WEAK</u>	<u>STRONG</u>
① { Polystyrene Vinyl	Excellent "	Excellent "
② { Methyl-Methacrylate Ethyl-Cellulose	Very Good "	Very Good "
③ { Phenolic: Acid & Alkali-Resistant Phenolic: Transparent	" "	Poor "
④ {	Urea	Fair "
	Aceto-Butyrate	"
	Phenolic: General Purpose	"
	Phenolic: Low-Loss	"
⑤ {	Phenolic: Heat-Resistant	"
	Phenolic: Shock-Resistant	"
⑥ Cellulose-Acetate	"	Very Poor "

^a Plastics Comparator, Copyrighted by Bakelite Corporation.

WATER ABSORPTION

(Immersion A.S.T.M.) (Lowest to Highest)

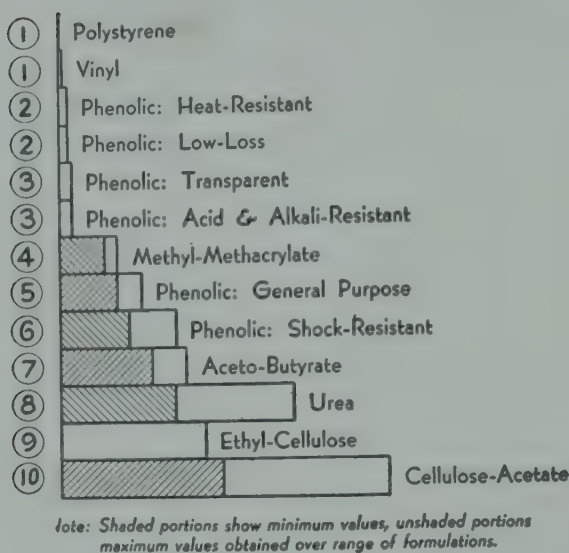


FIG. 5.20. (Plastics Comparator, Copyrighted by Bakelite Corporation.)

ozone. Polyisobutylene, on the other hand, has no unsaturation and is very resistant to the action of ozone.

The effect produced by increasing either the molecular size or the degree of cross-linkage in the molecule is comparable to that which would be expected from the discussion of solubility. In both cases the action of reagents becomes more sluggish.

Review Questions

1. What is the difference between the properties: specific gravity and bulk factor?
2. How is the specific gravity of a molding powder calculated?
3. If the force required to stretch a plastic strip $1\frac{1}{3}$ in. wide and $\frac{1}{2}$ in. thick to the breaking point is 9000 lbs., what is its tensile strength?
4. What factors may influence the tensile strength of a compounded mixture?
5. How is the value of elongation expressed? What is the effect of
 - (a) plasticizer
 - (b) filler
 - (c) chain length of the molecules
 upon it?
6. How can the energy required to rupture a plastic strip be determined?
7. What types of flexural strength are measured and why are they important?

8. What units of measurement are used to express:

- (a) elongation
- (b) modulus of elasticity
- (c) impact strength
- (d) Brinnell hardness
- (e) volume resistivity?

9. What is the specific heat of an unknown plastic if 73 g. requires 665 cal. to raise its temperature from 20° C. to 80° C.?

10. What is the main difference between the properties of

- (a) heat distortion point
- (b) continuous heat resistance,

and why are both important?

11. Define or explain the meaning of

- (a) dielectric constant
- (b) dielectric strength
- (c) power factor
- (d) arc resistance.

12. What factors are important in the solubility characteristics of a polymeric molecule? Explain.

CHAPTER VI

MACROMOLECULAR STRUCTURES

Previously, the structures of polymeric materials have been described as consisting of high-molecular weight molecules belonging to one or more of the types—linear, branched, or cross-linked. In view of the composition of these polymers, it is to be expected that many similarities exist between these molecular units and simple organic compounds. The primary valence bonds responsible for the arrangement and properties characteristic of organic molecules are known as homopolar covalences. These bonds are pictured as the mutual sharing of one or more pairs of electrons by the bound atoms ($C:C$). The fields of force represented by the electronic charges are distributed between the atoms involved. Although frequently distributed equally between carbon atoms, the proximity of functional groups may result in unequal sharing of these fields of force and the creation of polarities, e.g., ($\overset{+}{C} : \bar{C}$). In such cases the fields of force between carbon and some element other than carbon and hydrogen are always unevenly distributed, and this effect may be transmitted through the nearby portion of a carbon chain.

Much of the study of organic compounds has been involved with research into the characteristics of the homopolar covalent bond. The variations caused by shifting of the electrons, introduction of new substituents, subjection to external magnetic or electrical fields of force, and creation of additional electron pairs by elimination of substituent groups with resultant formation of double or triple bonds are several of the effects which have been studied. The knowledge gained in the study of relatively simple organic molecules has been and is being used to determine the geometrical structures of polymers.

The principal methods applied to the study of molecular structure are:

X-ray and cathode ray measurements

Evaluation of Dipoles (Polarizability)

Infra-red, Raman and band spectra.

Interatomic Distances.—The distances between neighboring atoms may be calculated by the use of X-ray or cathode ray measurements.

Results indicate the fundamental rule that valence distances are relatively constant. The distance separating the two constituent atoms in C—C, C=C, C=O, C—O, C—S, and other groupings remains fairly constant regardless of the compound in which the bond exists. Some variation has, however, been encountered. The presence of different substituents on the atoms involved may cause repulsions or attractions of the neighboring parts of the molecule. These, in turn, result in modification of the bond distances.

Correlation of bond strengths with bond distances has shown that a definite relationship exists. Variation of interatomic distances with variation of substituents accounts in some measure for differences in behavior encountered in the reactions and properties of organic compounds. Some typical atomic distances are listed in Table I-6.

TABLE I-6. A FEW IMPORTANT ATOMIC DISTANCES IN ORGANIC MOLECULES ^a

Linkage	Substance	Distance in Å
C—C aliph.	Ethane	1.56
	Cyclohexane	1.53
C—C arom.	Benzene, liquid	1.36
	Benzene, vapor	1.39
C=C	Ethylene	1.30
C≡C	Acetylene	1.19
C—H	Methane	1.08
	Ethylene	1.04
C—F	Methyl fluoride	1.43
C—Cl	Methyl chloride	1.86
C—Br	Carbon tetrabromide	1.93
C—I	Carbon tetraiodide	2.12
C—O	Methyl alcohol	1.46
C=O	Formaldehyde	1.19
C—N	Hydrogen cyanide	1.15–1.17
C≡N	Cyanogen	1.18
H—O	Water vapor	1.02
H—N	Ammonia	1.02–1.06

^a Mark, *Physical Chemistry of High Polymeric Systems*, High Polymers, Vol. II, p. 12, Interscience Publishers, Inc., New York, 1940.

Bond Angles.—The valence bond angles between the atoms in organic compounds, like the bond distances, are relatively constant, but dependent on the atoms involved. The fact that the valences of a carbon atom are directed toward the corners of a tetrahedron is well known. The angles formed between neighboring carbon atoms

or carbon and any different atom are approximately constant. However, these angles will vary more or less, depending on the nature of the attached atoms or groups. In water, for example, the oxygen valence angle is 105° instead of the theoretical value of 90° . The mutual repulsion of the two hydrogen atoms is responsible for an enlargement of the theoretical angle. If the hydrogen atoms are replaced with methyl groups, the valence angle is 111° , while replacement with two phenyl groups yields diphenyl ether, in which the valence angle of oxygen is 128° . Table II-6 contains some interesting valence bond angles.

TABLE II-6. BOND ANGLES IN SOME ORGANIC MOLCULES ^a

Substance	Bond	Angle of Bond
H ₂ O	H—O—H	105°
(CH ₃) ₂ O	C—O—C	111°
(C ₆ H ₅) ₂ O	C—O—C	128°
H ₂ S	H—S—H	92°
(C ₆ H ₅) ₂ S	C—S—C	113°
H ₃ N	H—N—H	108°
(CH ₃) ₃ N	C—N—C	108°
H ₄ C	H—C—H	110°
Propane	C—C—C	$111^\circ 30'$
Isobutene	C=C—C	$124^\circ 20'$
C ₂ H ₂	H—C≡C	180°
C ₆ H ₁₂ N ₄	N—C—N	110°

^a Data taken from Mark and Raff, *High Polymeric Reactions*, High Polymers, Vol. III, p. 14, Interscience Publishers, Inc., New York, 1941; and from Mark, *Physical Chemistry of High Polymeric Systems*, High Polymers, Vol. II, p. 16, Interscience Publishers, Inc., New York, 1940.

It has been calculated that the deformation of a bond angle to the extent of 10 degrees requires the absorption of 1,000–2,000 calories per mole, whereas an energy absorption of 10,000–100,000 calories per mole is necessary to stretch the interatomic bond distance by 0.1–0.3 Å. From these figures, it is obvious that the deformation of bond angles will occur more frequently and to a greater extent than the changing of interatomic distances. To put it another way, bond distances are relatively more constant than bond angles.

Internal Motions of Molecules.—Although it might be expected from these figures that the unit portions of each molecule are rigidly held in definite positions relative to one another, it is found that the geometrical relationships of organic molecules, and consequently

certain properties, depend upon the constant movement of the parts. The atomic arrangements of the molecule are subject to *oscillation* and *rotational* changes with respect to one another. In the case of oscillations, the change may be evident by alteration of the distance separating atoms. That is, atoms which are chemically combined may oscillate along the direction of the valence axis connecting them. This type of movement is referred to as valence oscillation. The motion referred to as break oscillation, on the other hand, results from the oscillating change of the valence angle. Rotational motion may occur in organic molecules because of the ease with which rotation about the C—C, C—O, or C—N bonds takes place. Both oscillation and rotation changes are determined by a study of infra-red absorption spectra, Raman spectra and emission spectra in the visible and ultra-violet regions. These internal motions do not result in any appreciable change in the total energy of the molecule. The energy differences which exist between different forms result in preferential or more stable forms, but these energy levels are not sufficiently different to materially affect the total energy. The movements result from thermal effects due to collisions. Consequently their dependence upon the temperature is evident.

Oscillations.—Measurement of oscillation behavior by means of Raman absorption spectra has shown that definite frequency values may be used to describe the oscillatory movement. In the Raman effect, light of a given wave length is sent through the molecule. A portion of this light energy is absorbed in causing oscillation of the atoms connected by a certain bond. The remainder of this light energy is then emitted as light of longer wave length. The difference in frequencies of the original light used and the emitted light is known as the Raman shift and is usually expressed as reciprocal centimeters. Specific Raman shift values have been determined for a large number of atomic linkages. Since these values are quite independent of the composition of the rest of the molecule, they are of considerable value in determining the structure of molecules. A table of Raman shift values for several common organic linkages is found in Gilman's Organic Chemistry.¹ Comparative study has shown that the effect of substituents on the atoms which form the bond being studied is negligible in the case of valence oscillation; the Raman shifts of $\text{ClCH}=\text{CHCl}$ and $\text{Cl}_2\text{C}=\text{CHCl}$ are 3078 and 3082 cm^{-1} respectively. When break oscillation is involved, smaller Raman shifts are obtained, and these vary with the nature of the substituent groups and the

¹ Gilman, *Organic Chemistry*, An Advanced Treatise, Vol. II, 2nd ed., p. 1777, John Wiley & Sons, New York, 1943.

size of the molecule. From these values it is possible to calculate the energy necessary to cause deformation of the bond angle and to estimate the molecular size of a polymeric molecule.

Rotational Motion.—Rotation about the C—C bond is a fundamental concept of organic chemistry. All possible configurations are theoretically capable of existence as the atoms rotate relative to one another. When, however, the carbon valences are saturated by other atoms, mutual attraction or repulsion of the connected atoms may be sufficient to cause appreciable energy differences between possible forms. In ethane, $\text{CH}_3\text{—CH}_3$, each carbon atom is saturated with three hydrogen atoms. It has been found that an energy trough exists when the carbon atoms are so rotated that the hydrogen atoms are at 60° angles with one another. Energy peaks occur when the hydrogen atoms are directly superimposed on one another in space. This is true because repulsion of the hydrogen atoms must be overcome before this form can be realized. These two extremes

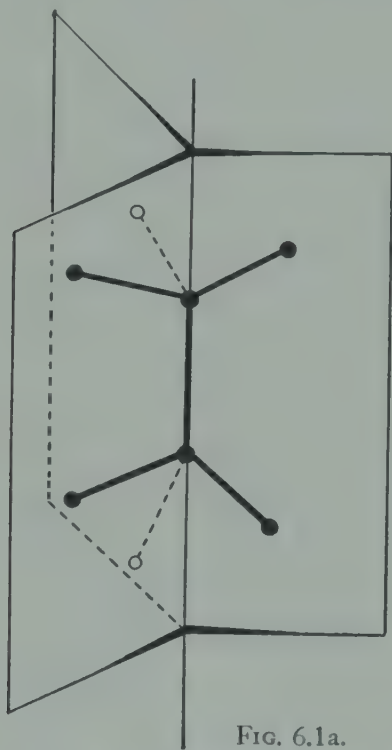


FIG. 6.1a.

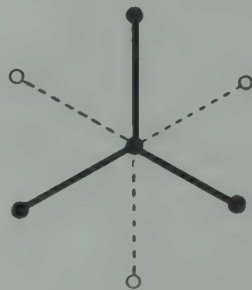


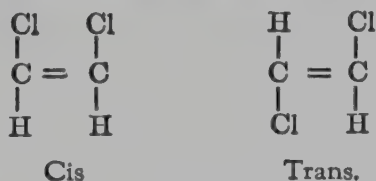
FIG. 6.1b.

FIG. 6.1a. The hydrogen atoms of one methyl group are directly above the hydrogen atoms of the other methyl group. (Mark, *Physical Chemistry of High Polymeric Systems*, High Polymers, Vol. II, p. 56, Interscience Publishers, Inc., New York, 1940.)

FIG. 6.1b. The molecule is viewed along the carbon axis and the hydrogen atoms of the two methyl groups appear at 60° angles to each other.

are pictured in Figures 6.1a and 6.1b. Thus, although free rotation is theoretically always possible about singly-linked carbon atoms, the motion is often restricted by the effect of substituents involved. Rotation still occurs to some extent and all possible configurations between the two extremes may be realized. However, the major portion exists in the configuration having the lowest energy.

When only hydrogen atoms are concerned, all configurations in which the atoms are rotated at 60° relative to one another are identical. When a chlorine atom is joined to each carbon atom as in 1,2-dichloroethane ($\text{CH}_2\text{ClCH}_2\text{Cl}$) two distinct isomers may be expected. The cis form, with the chlorine atoms on the same side of the valence axis, and the trans form, with the chlorine atoms on opposite sides of the valence axis, are theoretically possible. These rotational isomers do not exist in equilibrium because repulsion of the chlorine atoms in the cis form makes the trans form preferable. Even in this case, however, the geometrical structure is not one of rigid trans configuration, for the molecule may occasionally vibrate from a trans configuration to a cis configuration and thence to a trans configuration. A greater degree of rigidity is realized when the carbon atoms are joined by a double bond as in 1,2-dichloroethylene, $\text{ClCH}=\text{CHCl}$. The restricted rotation accounts for the existence of both cis and trans forms as stable configurations.



The relationship of atoms in space is thus a characteristic which is dependent upon the rotational motion of the parts involved. The existence of preferable positions often accounts for the polarization of the organic molecule. The permanent dipole moment is often directly dependent upon the configuration of the atoms in space. Since the existence of a dipole is due to the fact that the centers of gravity of the negative and positive charges in the molecule do not coincide in space, it is not surprising to find that a symmetrical

molecule such as trans dichloroethylene $\begin{array}{c} \text{H} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{H} \end{array}$ has a zero dipole moment whereas cis dichloroethylene has a moment ($\mu \times 10^{18}$) of 1.9.

Geometrical Structure of Polymeric Molecules.—In constructing a molecular model of a polymeric macromolecule the broad general-

izations governing the geometrical structure of simpler organic molecules must be applied. It must be remembered, however, that the influence of neighboring atoms and substituents is often different in the case of polymeric bodies because of the phlegmatizing effect of the chain size. Also, as the distance between the effective groups along the chain becomes increasingly great their effect upon one another decreases.

The molecular model may first be constructed by making use of interatomic distances and valence angles, the chemical composition of the polymer, (both qualitative and quantitative), the composition of the monomeric material and the type of polymerization involved. The polymer is pictured as a rigid, straight chain extending to the

limits of its molecular length. When such a form is depicted, however, no allowance is made for internal molecular motion. It is believed that the polymeric molecule is a shifting, kinked or coiled chain in which the more probable shapes are formed but not rigidly maintained. The fact that many forms have equal energy values and the fact that random arrangement into preferred forms occurs, account for the existence of many configurations for a single chain. It is, therefore, impossible to refer to rigid configurations. The chain is described by Mark² as being in "constant sinuous motion" and thus resembling a "caterpillar" rather than a "pencil." The maximum elongation of the chain is rarely reached because this form is only one of a multitude of possibilities. The existence of substituent groups (CH_3 , Cl , OCOCH_3 , etc.) along the chain accounts for the predominance of preferred forms of rotation isomers. The existence of two forms—cis and trans—in the case of iso-

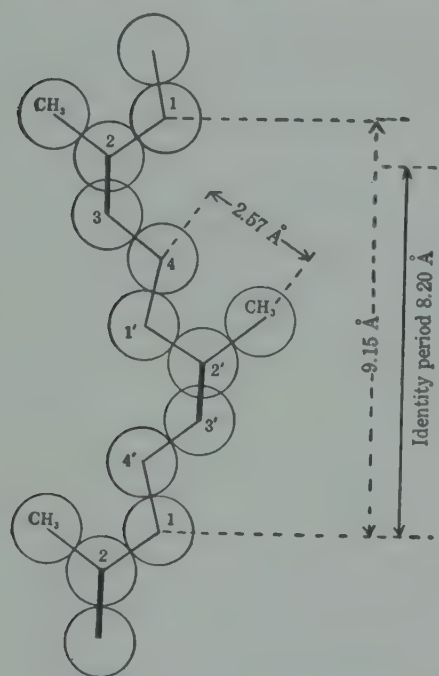


FIG. 6.2. Rubber chain stretched out flat; the identity period is greater than that observed. (Meyer, *Natural and Synthetic High Polymers*, High Polymer, Vol. IV, p. 128, Interscience Publishers, Inc., New York, 1942.)

prene polymers (rubber and gutta percha) has been discussed (page 38). The atomic model of the rubber chain is pictured in Figure 6.2, and the

² Mark, *Physical Chemistry of High Polymeric Systems*, High Polymers, Vol. II, p. 71, Interscience Publishers, Inc., New York, 1940.

theoretical and observed identity periods are shown. The fact that the observed identity period, 8.20 Å, is smaller than the theoretical value, 9.15 Å, which may be calculated from a flat model, indicates that some kinking of the rubber molecule occurs in its normal state. The effect of rotational hindrance caused by the presence of double bonds, large side-groups, or the interference of neighboring molecules often causes unpredictable behavior.

Macro-Structure of the Solid State.—The behavior of polymeric molecules and their role in the structure of matter are determined by a number of variable factors. The average molecular weight, the distribution ratios of the multi-sized chains, the forces existent between chains, the size of substituent groups, the rotational motion within the molecule, and the state of matter in which they exist are several of the factors which control the intermolecular relationships. Measurements of dipole moments, study of X-ray and absorption spectra data, and determinations of molecular weights are the most popular methods of investigation. Some of these factors are discussed more fully.

Molecular Weight.—Probably the most important structural characteristic of plastics, one which, in turn, controls a wide range of other properties, is that of *molecular weight*. The two principal features of macromolecules which make the determination of their molecular weights difficult have already been mentioned. Both may be summarized by the work "complexity"; complexity of form (linear, branched, and cross-linked polymers) and complexity of size distribution. Since the molecular growth of any polymeric substance may vary between wide limits, the experimentally determined molecular weight is really an *average value* of the molecules present in the particular sample used. In spite of the difficulties, approved and proven methods have been developed. The molecular weights of simple, low molecular weight organic compounds may be determined by using the common methods of change in freezing point or boiling point. The success of both depends on dissolving a sufficient number of solute particles to cause an appreciable change in the physical constants of the solvent. In the case of a polymeric material, however, a very large amount of solute must be dissolved before a sufficient number of particles is present to cause an appreciable change in either the boiling point or the freezing point. Limited solubilities, viscous solutions and association of molecules in more concentrated solutions are among the difficulties encountered.

When the necessity for new methods was thus indicated, the problem was approached from the viewpoint of either the size or the

weight of the molecules, rather than depending on the number of particles which might be dissolved. At present, there are three general methods which are in common use. They are:

1. Osmotic pressure, a property which depends on the number of dissolved particles;
2. Ultracentrifuge, a method which depends on the weights of the polymeric molecules;
3. Viscosity in solution, a property which depends on the size and shape of the macromolecules.

Osmotic Pressure.—If a solution of a polymer is separated from the pure solvent by a semi-permeable membrane (i.e., one which is permeable to the solvent molecules, but not to the solute molecules), the solvent will diffuse into the solution, thereby making the solution more and more dilute. This dilution of the solution can be prevented by the application of pressure, and the pressure required is known as the osmotic pressure of the solution. This property depends upon the number of dissolved particles and is independent of the chemical composition of those particles.

The molecular weight can be calculated from the following equation

$$PV = \frac{g}{m} RT$$

where P = osmotic pressure in atmospheres

V = volume of solution in liters

g = weight of solute in grams

m = molecular weight

R = gas constant, 0.08206 liter-atmosphere per degree

T = absolute temperature.

When osmotic pressure is used to determine the molecular weight of linear polymers, a correction is usually necessary. Ordinarily the equation holds true only at very great dilutions and only small variables are introduced when determining values of low molecular weight compounds or spherical molecules. As soon as the concentration of many linear polymer solutions is raised sufficiently to give a measurable osmotic pressure, the errors due to the space occupied by the solute and the attraction between molecules become appreciable.

Since osmotic pressure is directly proportional to the number of dissolved particles and since the number of dissolved particles, in the case of solutions of polymers, is relatively quite small, the osmotic pressure is usually measured in millimeters of water instead of either atmospheres or millimeters of mercury. The equation given above

can be changed to the following form:

$$M = \frac{2.31 \times 10^5 (1 + 0.00367t) C}{\bar{P}}$$

where M = molecular weight

t = Centigrade temperature

C = concentration of solution in grams per liter

\bar{P} = osmotic pressure in millimeters of water.

This equation holds only at infinite dilution, when the concentration equals zero. While this condition is impossible experimentally, it can be obtained graphically by making use of an expression proposed by Ostwald, namely:

$$\bar{P} = ac + bc^2 \quad \text{or} \quad \frac{\bar{P}}{c} = a + bc$$

where

$$a = \frac{2.31 \times 10^5 (1 + 0.00367t)}{M}$$

The osmotic pressure is then determined experimentally at several different concentrations, and the results are represented graphically by plotting \bar{P}/c against c . If the resulting curve is extrapolated to zero concentration, an hypothetical value will be obtained for \bar{P}/c . This graphically determined value may be used for " a " in the equation,

$$a = \frac{2.31 \times 10^5 (1 + 0.00367t)}{M}$$

and the molecular weight can then be calculated.

Ultracentrifuge.—Above a certain limit, in spite of the corrections introduced, the method of osmotic pressures produces less reliable results than those determined by the use of the ultracentrifuge. The principle upon which this method is based is that under the effect of force of gravity, particles will be distributed according to their weight. If the particles being examined are molecules, the vertical distribution of the particles will be proportional to their weights, i.e., the high molecular weight particles will be nearer the bottom and the particles having the smaller molecular weight will be at the top. Under the influence of the ordinary gravitational force, the distribution of particles is not sufficiently sensitive to permit accurate determination of the concentrations of the particles at different levels. In such cases, the gravitational force may be

increased up to one million times its ordinary value by the use of a high-speed *ultracentrifuge*. This method of separation and determination of molecular weights was first investigated and developed by Svedberg and his collaborators.

The actual determination consists of submitting the solution of polymeric material to the high gravitational field and measuring the concentration gradients after a regulated period of time. Thus, the concentration increment at a definite distance from the axis of rotation may be accurately measured by such an optical method as absorption (colored or ultraviolet) or refractive index.

The process of centrifuging and measurement continues until an equilibrium between sedimentation and thermal agitation results. Under these equilibrium conditions the molecular weights of the dissolved particles may be determined by the application of the formula:

$$M = \frac{2 RT \ln C_2/C_1}{(1 - V\rho)\omega^2(X_2^2 - X_1^2)}^3$$

where C_1 and C_2 are concentrations determined at the points X_1 and X_2 distances from the rotation axis, V is the partial specific volume of the solute, ρ is the density of solvent, and ω is the angular velocity.

An added advantage of this method is the fact that the homogeneity of the sample may also be tested. Thus, by determining the molecular weight at various distances from the rotational axis, an accurate description of both quantity and distribution of molecular weights may be deduced. Data for the distribution curve described on page 50 are often obtained by this method.

A different, newer procedure involving the use of the ultracentrifuge is a measurement of the *rate* of sedimentation in the centrifuged tube. This process is carried out by determining the rate of diffusion of the dissolved particles into pure solvent in a centrifuge tube. The difficulty encountered in the application of this process to chain polymers, however, is that the heterogeneity of particle size causes an indistinct boundary between solution and solvent. A greater degree of centrifugal force is necessary for accurate measurement in the latter case. Other drawbacks include the absence of any estimate of homogeneity in the sample and the necessity of testing polymeric solutions of extreme dilution. It is only in very dilute solutions that the linear molecules are sufficiently separated to exist as independent molecules.

³ Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 17, Interscience Publishers, Inc., New York, 1942.

Viscosity in Solution.—The third and probably the most widely used method of determining molecular weights is by a correlation of molecular weights with the viscosities of solutions of linear polymers. Although other workers had previously indicated that there was some relationship between viscosity and molecular weight, a definite mathematical relationship was first proposed by Staudinger⁴ in 1926.

The widespread application of Staudinger's method to polymeric substances required, first, a consideration of the physical shape of the macromolecules involved. Many types of spherical molecules of varying sizes and weights are found among macromolecules. Research on the dependence of viscosity on molecular weight indicates, in the case of spherical molecules, that the viscosity is dependent only on the number of particles (i.e., concentration). Hence, viscosity measurements cannot be applied in such cases, for only those types which produce viscosities which vary with particle size and mass are suitable.

The remaining divisions of polymeric substances are represented by the *long-chain molecules*. When in solution, the viscosity of such molecules may be shown to be due to the presence of either:

- (a) association colloids or
- (b) molecular colloids.

In the former, the dissolved particles have the power of aggregating into micelles. The behavior in solution is then due to the presence of these associated groups. When the concentration of a solution is reduced to a minimum, however, the tendency for such formations is slight and most types of macromolecules are included in the category of molecular colloids.

The viscosity effect of these linear polymers is ascribed to the fact that the polymers may be extended and, by rotation about mean positions, a cylinder of effective volume may be created. This cylinder represents, therefore, the space occupied by the chain polymer in solution.

The mathematical relationship between viscosity and molecular weight is expressed by the following formula:

$$\frac{N_{sp}}{C} = K_m M$$

in which C represents the basic concentration in terms of moles of the repeating unit (i.e., moles of isoprene (C_5H_8) in the case of

⁴ Staudinger, *Ber.* **59**, 3031 (1926).

rubber), M is the desired molecular weight, K_m is a constant which must be calculated for each type of compound in each particular solvent, and N_{sp} is recognized as the specific viscosity. The latter term is computed from the relative viscosity as follows:

$$N_r = \frac{t(\text{solution})}{t(\text{solvent})} \quad (t = \text{time of flow through standard orifice})$$

$$N_{sp} = N_r - 1$$

Theoretically, close agreement of molecular weight values obtained by different methods might be expected. However, variations of as much as 100% in the weights determined by osmotic pressure and viscosity methods have been encountered. The difficulties of maintaining accurate measurement control and agreement with theory in the case of osmotic pressures have been mentioned. Certain fundamental objections have also been encountered in the application of Staudinger's viscosity method. The most fundamental objection is that the ratio N_{sp}/C has been shown to vary extensively, even at extremely great dilutions. The ratio has been replaced for most practical work, therefore, by the term "*limiting viscosity*" represented by:

$$\frac{N_{sp}}{C}, \quad \text{where} \quad \lim_{C \rightarrow 0}$$

The figure is, therefore, the extrapolated ratio at zero concentration.

Other objections are largely dependent upon the physical configuration of these chain polymers in solution. Proof that an extended form is always assumed by the polymer molecule is lacking. Solvation of the polymer will yield incorrect results. Variation in degrees of branching which might occur in polymer structures is likewise productive of false results. The latter effect is troublesome for two reasons: first, branching alters the true cylinder calculated as the effective volume of a chain polymer, and, secondly, branching causes changes in the K_m constant. This figure is determined by a correlation of the viscosities in solution of low members of an homologous polymeric series with their molecular weights which may be determined by some other method. When the structure of higher members differs greatly from that of the lower members, the viscosity method gives inaccurate results.

Finally, caution must be exercised in attempts to compare the viscosity molecular weights with those determined by other methods. The former are known as the *weight average molecular weights* while

the latter are spoken of as the *number average molecular weights*. The difference between the two is attributed to the fact that polymeric materials consist of distributions of molecular weights with molecules of high molecular weight playing a predominantly greater part in determinations of viscosity while those of low molecular weight are of most importance in the determination of such characteristics as osmotic pressure and rate of sedimentation in an ultracentrifuge.

In spite of the variety of objections and unsolved questions facing the method of viscosity measurement, it is generally used for practical determinations because of its applicability in most cases. Many of the weight values recorded in the literature are determined by this method. Typical molecular weight values obtained by the viscosity method are given in Table III-6.

TABLE III-6. AVERAGE MOLECULAR WEIGHTS AND CHAIN LENGTHS ^a

Substance	Ave. Mol. Wt.	Chain Length in Å
Polystyrene	600,000	15,000
Polyvinylacetate	80,000	2,200
Rubber	125,000	8,100
Balata	50,000	3,400
Cellulose	120,000	3,900
Triacetyl Cellulose	103,000	1,900

^a Data taken from Staudinger *Die Hochmolekularen Organischen Verbindungen*, p. 104, Van J. Springer, Berlin, 1932.

Other Methods.—Although the three methods just described, osmotic pressure, ultracentrifuge, and viscosity, are of quite general application, there are other methods which may be used for the determination of approximate molecular weights. Thus, by a determination of such properties as density, index of refraction, or solubility of a series of compounds chemically similar to the polymer being investigated, some relationship between molecular weights and the values for each property may be deduced. By extrapolation of the curve relating molecular weights and physical property values to the value recorded for the polymer, an approximate molecular weight may be determined. This method is used extensively in hydrocarbon chemistry. In this way, the molecular weights of hydrocarbons containing 30–40 carbon atoms may be readily determined.

Occasionally, the molecular weight of macromolecules may be

polymerization. When the end groups in a polymer chain may be quantitatively estimated the molecular weight can be deduced. For example, if in a polycondensation the chain growth could only cease with a carboxyl group at either end ($\text{HOOC} \text{-----} \text{COOH}$), titration with alkali would permit calculation of the average weight of each chain.

Such general approximations as these are typical of methods which may be applied under certain conditions and in isolated cases.

Crystalline Structure.—The arrangement of the molecules relative to one another may be deduced from a study of the x-ray patterns of the polymer. First, from a knowledge of bond angles and distances, the number of possible configurations may be limited. Then, by measurement of the identity period (distance between identical atomic groupings in the chain molecule) the configurations may be further limited. Thus, in the polyisoprene chain the configurations of rubber and gutta percha are shown to have different identity periods. Rubber exists in a more or less folded form and thus possesses a shorter identity period.

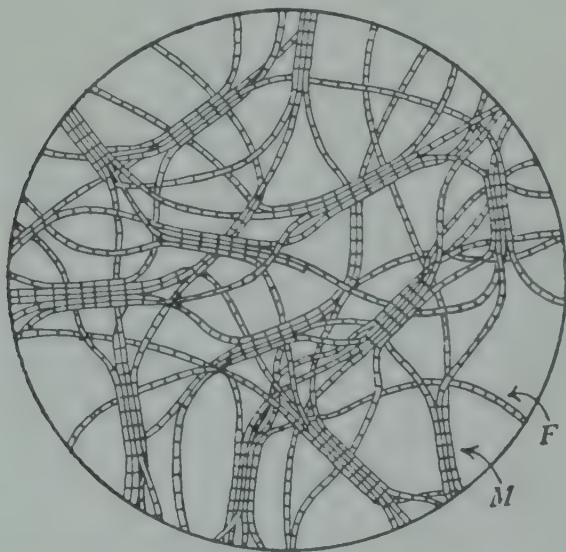


FIG. 6.3. Fringe structure of rubber after Herrmann and Gerngross. F, fringes; M, micelles (crystallites). (C. Houwink, *Elasticity, Plasticity and Structure of Matter*, p. 210. Courtesy of Cambridge (England) University Press.)

Knowledge of the chain symmetry and order then develops with continued study of the x-ray pattern into an understanding of crystalline measurement and the dimensions of the unit cell within the crystalline regions. Degrees of crystallinity, which may be varied

by alteration of the physical conditions, as by the stretching of rubber, may be measured for each polymer. Generally it is found that crystalline regions along the fiber axis exist with amorphous regions interspersed between them. The conception of "fringed micelles"⁵ has arisen to describe this irregular existence of crystalline and amorphous regions. The existence of fringed micelles is illustrated in Figure 6.3. The regions in which several molecular chains are lying side by side are the fringed micelles. At room temperature, the molecular oscillations of the chains prevent the fringed micelles from showing an x-ray diagram characteristic of an oriented structure. When the rubber is chilled, however, the molecular oscillations are reduced to such an extent that an x-ray diagram is produced. An x-ray diagram of frozen rubber is shown in Figure 6.4. Because of the random arrangement of the micelles in different planes, the x-ray diagram of frozen rubber resembles that obtained from a crystalline powder. However, when rubber is stretched, the micelles become oriented in parallel planes and a typical fiber diagram is produced. When the arrangement reaches a high degree of orientation, the dimensions of the unit cell may be measured along its three principal axes. Such data are obtained from a study of the intensity, shape, and order of the bright spots of the x-ray diagram.

The binding forces within the molecule are those of primary valence which are of the order of 20,000 to 200,000 cal. per mol.⁶ The intermolecular binding energy is provided by the secondary valence forces of molar cohesion. Typical values of representative atomic groupings are recorded in Table IV-6. These are of the order of 500-5000 cal. per atom⁶ or atomic grouping. These values are dependent upon the polarizability and permanent dipole moment of the grouping involved. It is found that for the most part the effects of the groupings are additive except in cases in which mutual interference may occur. As expected, therefore,

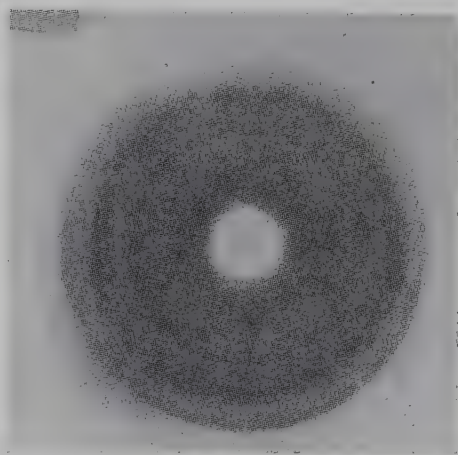


FIG. 6.4. X-ray diagram of unstretched frozen rubber, showing Debye-Scherrer-Hull circles. (Courtesy of Ernst A. Hauser, Massachusetts Institute of Technology.)

⁵ Hermann and Gerngross, *Kautschuk*, **8**, 181 (1932).

⁶ Mark, *Physical Chemistry of High Polymeric Systems*, High Polymers, Vol. II, p. 112, Interscience Publishers, Inc., New York, 1940.

TABLE IV-6. MOLAR COHESION OF DIFFERENT ORGANIC GROUPS ^a

Group	Molar Cohesion in cal. per mole	Group	Molar Cohesion in cal. per mole
—CH ₃	1780	—NH ₂	3530
=CH ₂		—Cl	3400
—CH ₂ —		Only approximately known	
=CH—	990	—F	2060
—O—		—Br	4300
—OH		—I	5040
=CO	4270	—NO ₂	7200
—CHO		—SH	4250
—COOH		—CONH ₂	13200
—COOCH ₃	5600	—CONH—	16200
—COOC ₂ H ₅			

^a Mark, *Physical Chemistry of High Polymeric Systems*, High Polymers, Vol. II, p. 113, Interscience Publishers, Inc., New York, 1942.

with an increase in molecular weight, the molar cohesion values will increase proportionally to chain length.

Effect of Elongation on Crystallization.—It is possible to correlate directly the effect of mechanical stress and degree of crystallization of an amorphous body by a consideration of how these properties are interrelated in the case of rubber. Emphasis is again placed on the fact that crystallization in this case is the production of an orderly arrangement of molecules by the application of an external force. As a strip of rubber is stretched it gradually changes from the amorphous state to the "crystalline" state. A discussion of the changes which take place during this extension period may be applied with slight modifications to other high-polymers. Two types of behavior may be evident, namely, elastic behavior and plastic behavior.

Elastic Behavior.—Elastic behavior is reversible in that the deformation is totally lost when the stress is removed. If the changes in percentage elongation are plotted against the stress applied, the

typical elastic behavior curve for rubber would show three definite stages.⁷

In the first stage, there is a moderate increase in percentage elongation with the first portion of stress introduced. This characteristic is true up to approximately 200% elongation.

In the second stage, a smaller stress causes a more rapid increase of elongation (over the same period). This holds while the elongation increases from 200% to 500%.

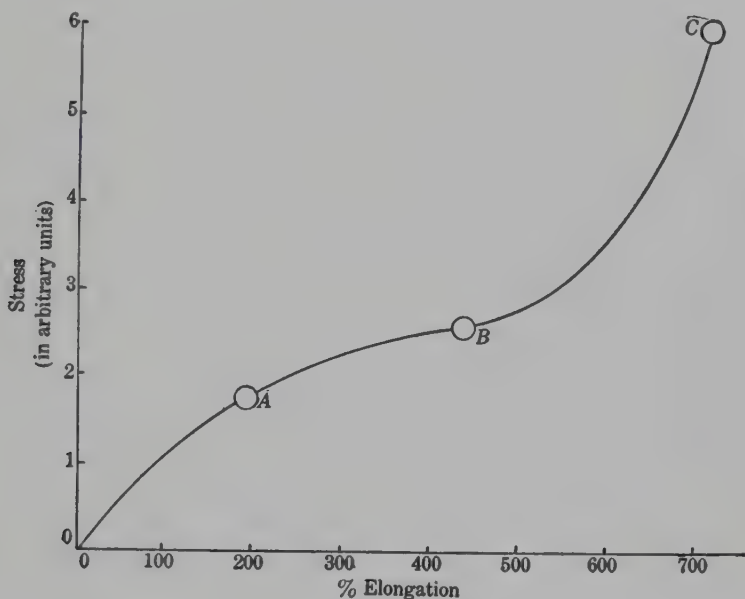


FIG. 6.5. Typical stress strain curve of rubber.
(Mark, *Ind. Eng. Chem.* **34**, 451, 1942.)

When the third stage is reached, a large increase in stress causes little or no increase in elongation. Figure 6.5 represents these three stages.

These changes may be explained by first picturing the long-chain polymers of rubber as being in a disordered, jumbled arrangement, with the existence of amorphous regions and of fringed micelles in unoriented form. (See Figure 6.3, p. 102). As the rubber is subjected to stress it elongates first by an uncurling and disentanglement of the linear polymeric fibers, causing increasing orientation of the micelles. As the chains reach their maximum length (200% elongation), the secondary valence forces aid crystallization. During this period the force required to bring about a proportionate elongation

⁷ Mark, *Ind. Eng. Chem.*, **34**, 449, 1942.

is less than that of the first portion of the curve. In other words, the modulus of elasticity (force required for definite elongation) diminishes from 10^6 – 10^7 dynes/sq. cm. to 10^4 dynes/sq. cm., because the cohesive forces within the macro-structure supplement the external stress during the second or crystallizing stage.

The last portion of the stress-strain curve is caused by the elongation or stretching of the crystallized elongated rubber. Under these conditions the degree of crystallization is approaching unity and the modulus may increase to 10^{10} dynes/sq. cm., because additional elongation is possible only by an elongation or stretching of the crystalline phase. Of interest in this respect is the fact that the degree of crystallization probably never reaches unity. The linear polymers in all cases appear to consist of a mixture of crystalline and amorphous phases. Each chain may consist of several regions in which a parallel arrangement or crystalline area exists and other areas which are of the disordered amorphous type.

Plastic Behavior.—When stretched beyond their elastic limit, high polymers exhibit a complex type of elongation known as plastic flow. With constant load above the elastic limit, the polymeric material undergoes a slow deformation which is not reversible. When the stress is removed the elongation due to elasticity is lost through recovery, but the portion due to plastic flow remains. Consequently the polymer does not return to its original dimensions and is said to have a *permanent set*. The extent of deformation is proportional to the amount of stress applied and the length of application.

Another type of relationship between deformation and recovery has been described by Leaderman.⁸ The effect is spoken of as *primary creep*. Under ordinary circumstances, application of stress or loading results in:

- (a) rapid elongation (elastic)
- (b) slow deformation (plastic).

(See page 67)

The rapid elongation is represented by OA in Figure 6.6, and the slow plastic deformation is represented by the curve AB . Removal of the load causes a partial rapid recovery which is equivalent to the original elastic deformation and is represented by BC . The slow recovery of most of the remaining deformation is represented by the curve CD . The vertical distance between O and D is the permanent set. However, if the cycle of stretching and recovery is repeated

⁸ Leaderman, *Ind. Eng. Chem.* **35**, 374 (1943).

with the same sample of material, it may regain the dimensions that it had at the beginning of the test. The results are represented graphically in Figure 6.7. Such a sample is referred to as being "mechanically conditioned" and "primary creep" is the term given to this "delayed elasticity." This phenomenon is observed only when the stress applied is not too great.

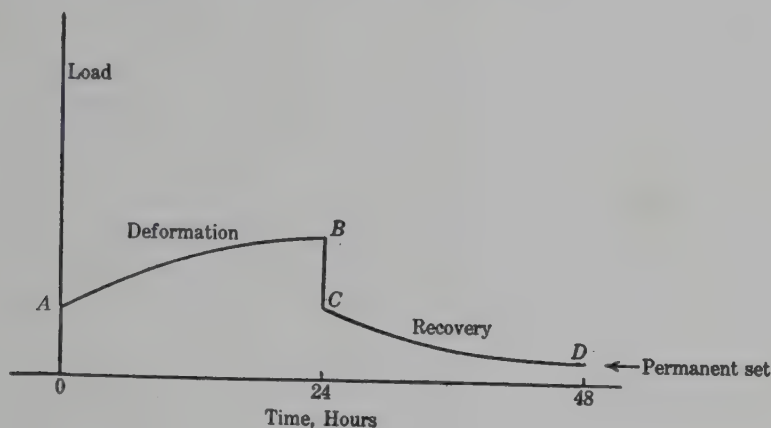


FIG. 6.6. Relationship between plastic deformation and recovery. (Leaderman, *Ind. Eng. Chem.*, 35, 375, 1943.)

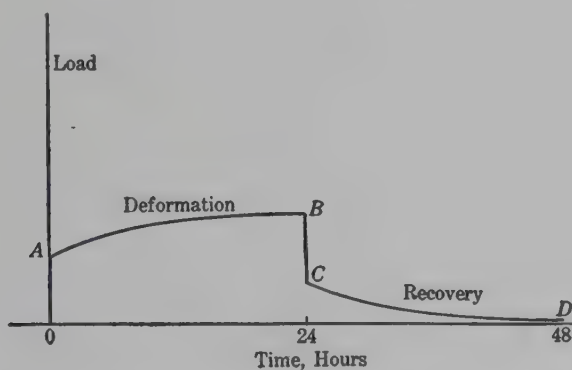


FIG. 6.7. Relationship between plastic deformation and recovery of a mechanically conditioned sample. (Leaderman, *Ind. Eng. Chem.* 35, 375, 1943.)

Effect of Temperature on Crystallization.—The effect of temperature on the ease of crystallization in high-polymeric materials is shown from a comparison of the stress-strain curves of rubber at different temperatures. As would be expected from kinetic considerations, low temperatures aid crystallization while higher temperatures have the opposite effect. In the typical stress-elongation curve of elastic behavior discussed above (p. 105), low temperatures tend to shorten the first portion of moderate increase of elongation with stress. Consequently, the second portion of the curve is

reached sooner, indicating that crystallization occurs more readily at lower temperatures.

The effect is due to the decreased kinetic energy at reduced temperatures. Under these conditions, the molecules more readily assume a parallel, orderly arrangement, and the secondary valence forces supplement the external stress in causing crystallization. At elevated temperatures the reverse is true. Higher kinetic energies hinder the formation of an ordered pattern, and the secondary valence forces do not enhance the applied stress to the same degree that they do when the kinetic energy is decreased.

Use of X-Rays in High-Polymer Structure Studies.—X-rays are, in effect, a form of radiant energy similar to light in their velocity, but of much shorter wave length. It is a well known fact that the wave length of ordinary light can be determined by the use of a diffraction grating made by scratching parallel lines on plate glass or by a pile of thin glass plates. The determination is possible because of the fact that the light waves striking the grating are diffracted, or for our purposes, reflected from the alternate, parallel zones. Because of this fact, Laue suggested that the orderly arrangement of the atoms or molecules within a crystalline structure might act as a diffraction grating for x-rays. Since the distances between the planes within the crystal are of approximately the same order as the wave length of the x-rays, the crystal acts as a three-dimensional optical grating for the reflection or diffraction of these x-rays. The intensity of the reflected light can be recorded on a photographic plate. In the Laue method, general x-radiation is used, which consists of x-rays having many different wave lengths. This produces a spot pattern with some bright and some dark regions, as illustrated in Figure 1.3, Chapter I, p. 9.

In addition to this first method of x-ray study of crystals, two other principal methods have been developed, namely the Bragg and the Debye and Scherrer methods.

Bragg's method makes use of monochromatic x-rays obtained by screening out the radiation of wave lengths which are different from that chosen. Analysis of the atomic planes of a crystal by this method depends upon rotation of a crystal in the path of the x-ray and determination of the angles of reflection at which intensified or constructive interference of the reflected light occurs. Intensification or brightness of reflection will occur at definite angles of the light to the face of the crystal, for it is only at these angles that light will be reflected from each of the internal planes in such a way as to reinforce that reflected from the other planes. When the angle of incidence

is such that the path of reflection from each successive atomic plane differs by an integral number of wave lengths, constructive reinforcement of the reflection occurs. Otherwise, light from one plane interferes with that from an adjacent plane and no brightness area results. The relationship used to determine the distance between planes is expressed as

$$n\lambda = 2d \sin \theta$$

in which,

n is a small integer equal to the number of wave lengths in the path of reflection between two successive atomic planes,
 λ is the wave length of the monochromatic x-rays used,
 d is the vertical distance between two crystal planes,
 θ is the angle of reflection.

By rotating the crystal and noting on the photographic plate the areas of intensified brightness for different values of θ , the values for n can be determined. Since the wave length, λ , is also known, the distance between the planes of the crystal can be calculated.

The tedious measurement of intensified reflection areas by rotation of a crystal are eliminated by the use of a crystalline powder. This so-called powder method was developed by Debye and Scherrer, who reasoned that because of the random arrangement of the particles of a finely powdered substance, all possible angles of incidence would be represented, and all of the reflection bands would be recorded on one photographic plate. This method has been of great value in the study of both synthetic and natural polymers.

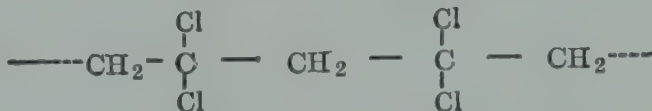
The x-ray pattern of amorphous substances is characterized by a halo with no evidence of rings or spots of well-defined intensity.

Most linear polymers of high molecular weight, when unstretched, exist in a disorderly non-crystalline structure with no planes present to act as optical gratings. When subjected to mechanical stress, however, crystallization is induced and intensified spots or rings appear in the diffraction pattern. Thus, unstretched rubber presents an x-ray pattern which consists only of a broad halo. When it is subjected to mechanical stress, however, intensified spots appear on the x-ray photographic plate. These become more regular and distinct as elongation and crystallization proceed.

Low molecular weight resins such as those obtained from coumarone and indene present x-ray patterns which show a regular recurrence of intensity bands, thereby indicating a partial crystalline arrangement.

X-ray studies made during the formation of a phenol-formaldehyde resin are particularly instructive. The fusible product, which is first formed and which is believed to consist of linear polymeric molecules, shows clear rings of diffraction planes when subjected to x-ray analysis. During the last stage of the reaction, when cross-linking occurs, the number of rings is reduced to one, the intensity curve gradually broadens and finally, a broad halo remains.

One of the most interesting and informative x-ray series is that which pictures the structure possibilities of polyvinylidene chloride.



The commercial polymer may exist in three degrees of crystallinity—amorphous, crystalline, and oriented crystalline. The form is predominantly dependent upon the previous treatment. By proper processing (as described on pages 307–309) any one of these three forms may be produced. The three types of x-ray diagrams are represented on p. 306.

Review Questions

1. Why is the study of interatomic distances, interatomic angles, and bond energies important in the study of organic molecular structure?

2. Explain the meaning of

- (a) oscillation energy
- (b) rotational energy
- (c) valence oscillation
- (d) break oscillation.

3. Describe a polymeric molecule briefly, making use of the concepts discussed in this chapter.

4. What is the principle upon which the ultracentrifuge method of determining molecular weights is based?

5. What objections have been raised to Staudinger's method of determining the molecular weight of polymers.

6. Explain the meaning of:

- (a) amorphous
- (b) crystalline
- (c) fringed micelles
- (d) primary creep
- (e) permanent set.

7. Summarize the crystalline and plastic properties of polymeric matter.

SECTION II
PLASTIC TYPES

CHAPTER VII

USE OF RESINS IN INDUSTRY

Historical.—The general use of plastics is almost as old as civilization, for when man first learned to utilize materials of nature, he originated the art of plastics. Down through the ages the category of plastic materials has included such otherwise unrelated materials as iron, steel, leather, rubber, wood, clay, glass and silk.

Developments of the past century, however, have resulted in the term "plastics" being used principally for those materials of synthetic origin which may be conveniently handled by the plastics art. Fundamentally, the field includes the two distinct classes of *natural* and *synthetic* materials. The natural plastics range from products with strong fiber-like properties to hard, brittle resins; from sticky, viscous gums to well-defined, difficultly-fusible solids; from resilient, elastic rubbers to readily-deformed asphalts or bitumens.

The synthetic plastics include either materials built up by chemical processes from non-resinous materials or products obtained by a chemical alteration of one of nature's polymeric bodies. The properties of these synthetic products also vary between wide limits. Synthetic plastics may be subdivided into the following groups:

- (a) Thermosetting types
- (b) Thermoplastic types
- (c) Cellulose derivatives
- (d) Protein plastics
- (e) Elastomer types
- (f) Miscellaneous.

Some overlapping of one basic plastic between two or more groups may occasionally occur. For example, the reaction between phenol and formaldehyde may be carried out with an insufficient amount of formaldehyde present, to form a thermoplastic resin. If an excess of formaldehyde is used, a thermosetting resin is obtained.

Both natural and synthetic plastics may be subdivided into two very broad groups, namely, diluent and film-forming resins. The diluent resins are brittle, friable materials such as rosin, gum Congo, or synthetic polymers obtained from coumarone and indene. Film-forming resins, on the other hand, possess characteristics of cohesive,

internal strength. Cellulose derivatives, rubber, and the synthetic elastomers are examples of this class.

The gradual development of the plastics industry may be traced, therefore, from its birth to its present position of great industrial importance. The stepping-stones of its rise may be enumerated as follows:

1. General use of natural products as rubber, shellac, sealing-wax, gums.
2. Discovery of effect of sulfur on rubber, i.e., vulcanization (Hayward and Goodyear 1839).
3. Production of cellulose nitrate—the original ivory substitute (Schoenbein 1846).
4. Importance of cellulose nitrate demonstrated and possibilities of industrial use became apparent when plasticized with camphor (Hyatt 1869).

TABLE I-7. CELLULOSE PLASTICS AND SYNTHETIC RESINS: UNITED STATES PRODUCTION, IN SPECIFIED YEARS, 1930 TO 1942 ^a
(In Pounds)

Year	Cellulose Plastics(a)	Synthetic Resins		
		Coal-tar	Non-coal-tar	Total
1930	14,645,002(b)	30,867,752	—	30,867,752
1933	14,398,184	41,628,485	3,571,717	45,200,202
1935	26,709,416	90,913,162	4,220,222	95,133,384
1938	23,712,723	106,923,244	23,435,408	130,358,652
1940	35,765,340	222,943,118	53,871,245	276,814,463
1941	53,433,787(c)	334,200,666	103,599,021	437,799,687
1942	32,711,245(d)	283,844,481(e)	142,886,625(e)	426,731,106

(a) Statistics for 1931–35 include only sheets, rods, and tubes; production data on molding composition were not available until 1938.

(b) Year 1931. Not available prior to 1931. Production in 1931 was principally nitrocellulose; only negligible quantities of cellulose acetate were produced before 1933.

(c) Beginning with February 1941, data do not include production of cellulose acetate safety-glass sheets.

(d) January–June 1942.

(e) Preliminary.

Source: Compiled by the U. S. Tariff Commission from official statistics of the U. S. Bureau of the Census, and U. S. Tariff Commission reports on Synthetic Organic Chemicals, United States Production and Sales.

^a Courtesy of United States Tariff Commission.

5. Discovery of less-flammable cellulose derivative—cellulose acetate (Schuetzenberger—approximately 1870).
6. Isolation of new type of plastic—casein from cow's milk (Childs 1885) and application to industrial use (Spitteler 1904).
7. Momentous discovery of application of phenolic resins by molding (Baekeland 1909).
8. Synthetic glass prepared from urea-formaldehyde reaction (Hanns, John 1917).
9. Utilization of light-stable, eye-appealing ureas in industry (approximately 1927).
10. Rapid advance, 1929–1944, in resin types: Polystyrene, polymethyl methacrylate, polyvinyls, nylon, synthetic rubbers—and improvement in industrial methods suitable for manufacture of processed goods.

The actual growth and development may best be traced by a comparison of production figures from 1931–1941 (Table I-7). If graphed, the values would show a sharp rise in production during the later years. There is no indication yet that this trend will be slowed or stopped.

Importance.—The importance of modern synthetic plastics in our daily lives is emphasized by the widespread application they enjoy. Reasons for such popularity are numerous, but a brief consideration of the properties of these materials is all that is necessary to understand the advantages resulting from their use in many cases. Thus, within this new class, plastics have arisen which are lighter than metals, more flexible than porcelain, tougher than wood, cheaper than ivory, and more workable than clay. The plastics differ from each other widely in their specific desirable properties, but the general advantages of the materials as a class are:

- Lightness
- Tensile strength
- Electrical resistance
- Heat resistance
- Chemical resistance
- Shock resistance
- Ease of processing
- Hardness
- Flexibility.

Combinations of such properties may be attained by the use of plastics either alone, after compounding, or after various physical

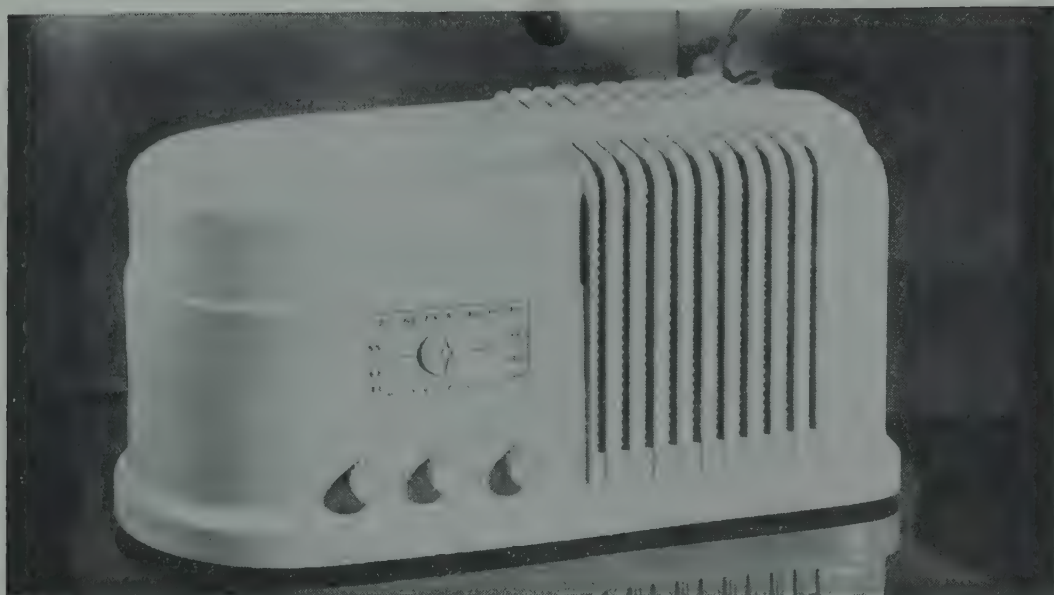


FIG. 7.1. Radio cabinet made from urea-formaldehyde resin. (Courtesy of American Cyanamid Company, Plastics Division.)

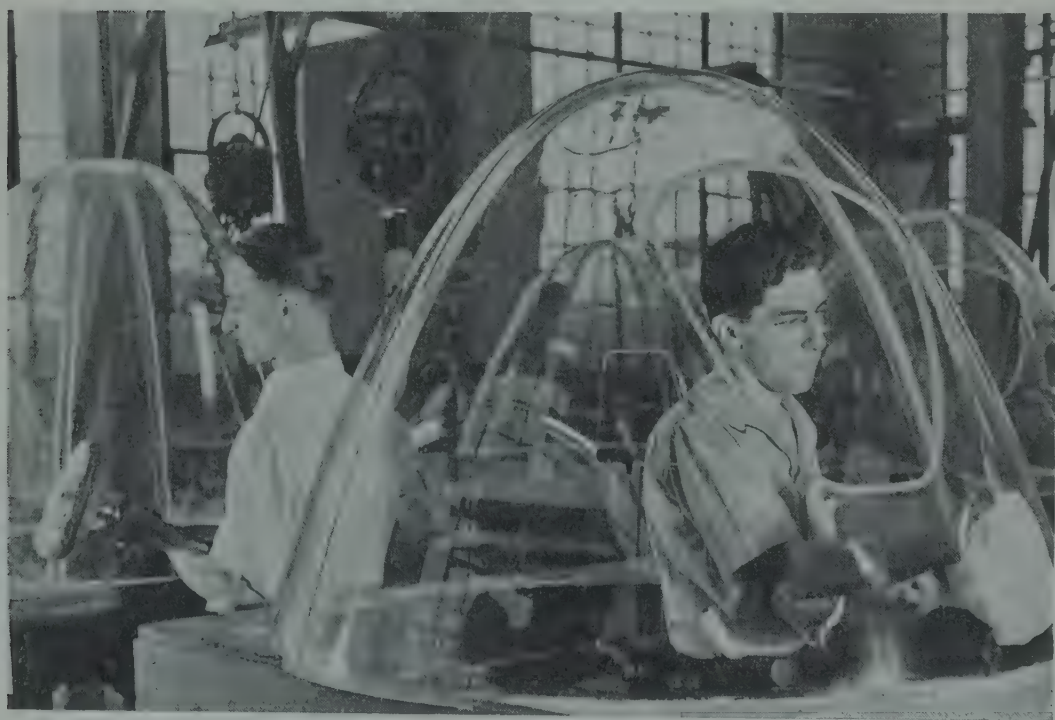
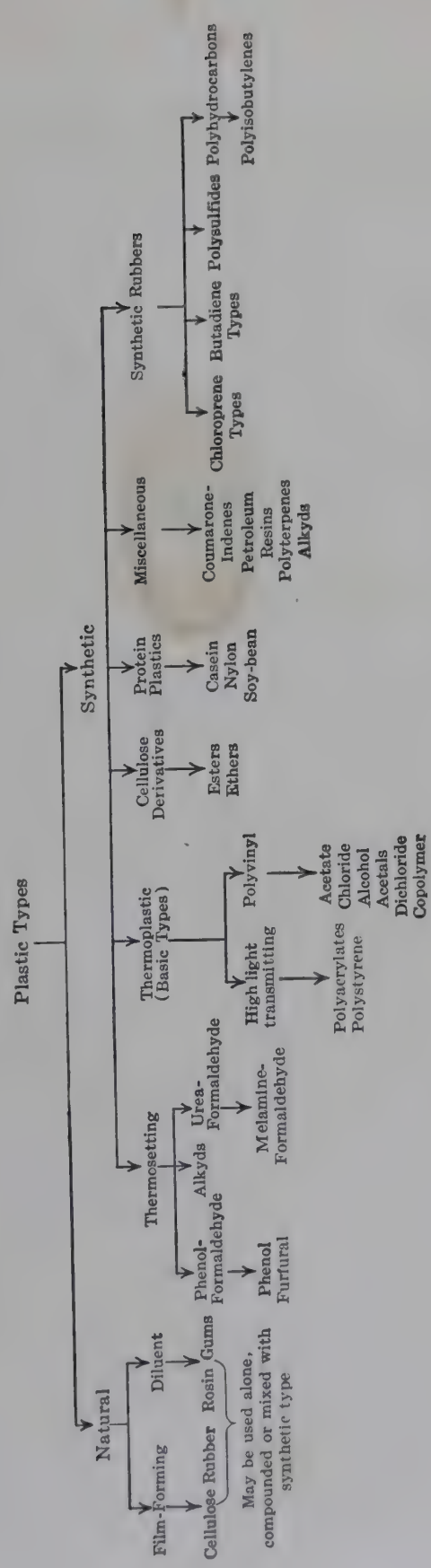


FIG. 7.2. Polishing and buffing Plexiglas bomber noses. (Courtesy of Rohm and Haas Company.)

TABLE II-7. CLASSIFICATION OF PLASTICS



operations of processing. The widespread possibilities result in many varied applications. A summary of representative uses includes: dresser sets, furniture table tops, refrigerator parts, distributor caps, steering wheels, dashboards, light reflectors, fish lines, upholstery, clothing, shower curtains, lamp shades, radio cabinets, shoe heels, paints, varnishes, abrasive wheels, safety glass, dentures, speed boats, wall paneling, advertising displays, wrapping paper, and garden hose.

Likewise, the application of plastics to weapons of offense and defense has resulted in innovations by the introduction of new combinations of properties, as, for example, the transparent noses of Plexiglas on the big army bombers. (See Figure 7.2.) The machinery of war now includes such plastic parts as: bomb releases, cockpit windshields, nose turrets, bulkheads, bomb fins, electrical housings, helmets, wire reels, microphones, cable coatings, raincoats, switch housings, and pistol grips.

The list of articles which may be produced by proper processing of plastics is in no way complete. The vision of future needs and attainments in the field includes total assemblies—planes, automobiles, boats, houses, furniture—constructed of plastics. The number and variety of plastics products now being produced will be far surpassed by those available after another decade or two of research and development in this field.

Resin Types in General Use.—The wide variety of applications indicates that there are several different types of resins available commercially. The more important classes of plastics are listed in Table II-7 in the appropriate subdivisions.

Typical Methods of Application.—The processing and application of synthetic resins have kept pace with their preparation and manufacture. Of the several processing methods useful in the plastics industry the most important and most widely used is that of *molding*. Other methods are rapidly becoming of major interest. Each will be discussed in a general way in order that references in the later text material will be understood. A more detailed discussion of these processes will be found in Section III.

The art of molding plastics, i.e., shaping the basic materials by suitable application of heat and pressure, is represented by several types of processing.

Compression Molding.—This is a general method useful for thermosetting or thermoplastic types alike. In principle, the technique applied consists merely of simultaneously heating a plastic and forcing it by pressure into the contours of the mold being used.

Since heat causes the thermosetting types to harden, the molded form may be removed while the mold is hot. The thermoplastic types, on the other hand, remain soft at elevated temperatures and, therefore, the mold must be cooled before removal. The three essential steps in the process are shown in Figure 7.3. In the first

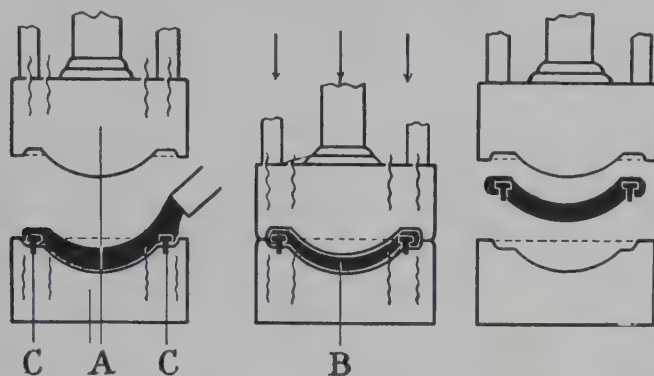


FIG. 7.3. Compression molding. (Courtesy of Monsanto Chemical Co.)

diagram, the molding powder is loaded into the mold (*A*), after careful positioning of the inserts (*C*). The mold is closed and heat and pressure are applied simultaneously, causing the plastic (*B*) to soften and flow to all parts of the mold cavity. The third diagram shows the molded piece.

Injection Molding.—This method, in the past, has been useful only for thermoplastic types. Revolutionary changes of technique

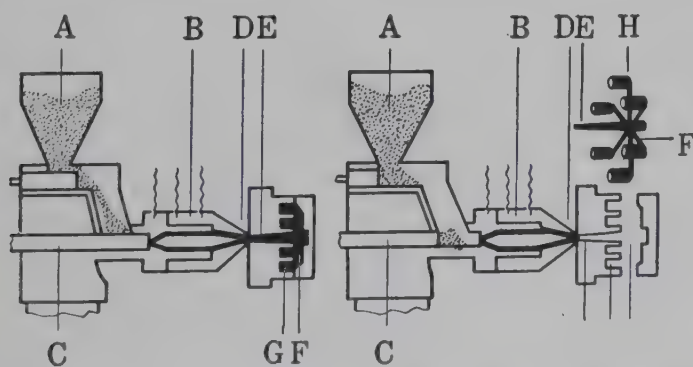


FIG. 7.4. Injection molding. (Courtesy of Monsanto Chemical Co.)

and machines have lately introduced the possibility of using thermosetting types. As Figure 7.4 illustrates, the resin (*A*) is first softened while passing through a heating chamber (*B*), and is then forced by the ram (*C*) through the nozzle (*D*) into the mold cavities (*G*). The second diagram represents the ram retracted so that more molding

powder can be introduced into the heating chamber. At the same time, the mold is opened and the molded piece is ejected. This molded piece generally consists of a sprue (*E*), several molded articles

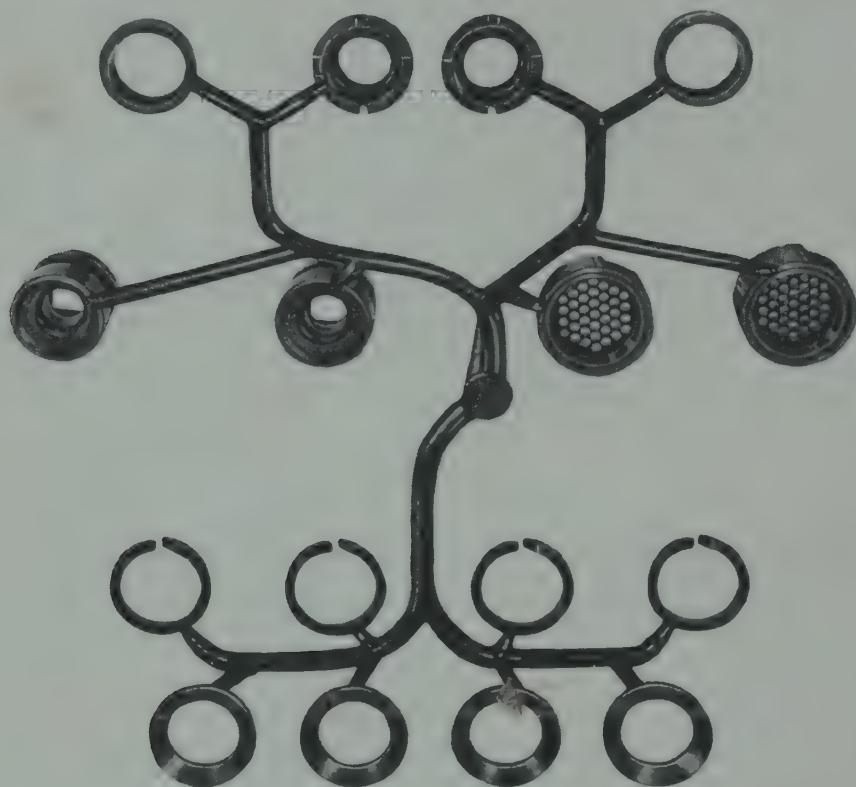


FIG. 7.5. Injection molded piece consisting of parts for a fire extinguisher pump. Note the relationship of runners and molded parts. The complexity of design is illustrated by the strainers and threaded parts. (Courtesy of Santay Corporation.)

(*H*) and runners (*F*) which connect the sprue to the molded articles. Again, the temperature of the mold must be regulated according to the requirements for the product, and the properties of the resin being processed. It is generally cool if applying a thermoplastic resin; hot when a thermosetting resin is being used.

Extrusion.—The actual processing techniques of extrusion are very nearly those of injection molding. The only fundamental difference between the two is that, in this case, the fabricated form is produced in a continuous sheet, rod, or tube by the softened plastic being continuously forced from the orifice of the heating chamber, as shown in Figure 7.6. The plastic is fed from the hopper (*A*) into the heating chamber (*B*) where it is moved along by the worm screw (*C*). As the plastic is forced out of the heating chamber it

goes through a die (*D*) which produces the desired shape. The diagram also shows the material being led onto a conveyer (*E*) on which it is cooled and cut (*F*) to desired lengths.

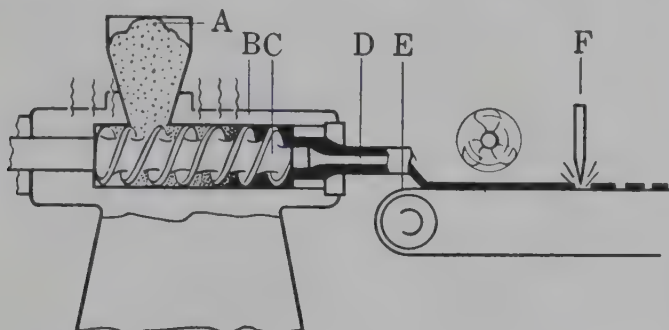


FIG. 7.6. Extrusion. (Courtesy of Monsanto Chemical Co.)

Transfer Molding.—Briefly, this method is the application of injection molding technique to compression molding. Of limited application, its main features are pre-softening of the molding powder followed by shaping of the plastic when it is forced into the mold cavity by the upper portion of the mold acting as the piston. The mechanical arrangement is like that used in compression molding, but the basic method is that of injection molding. Figure 7.7 shows the plastic material after it has been forced through the gate into the lower cavity. The cull or residual plastic is shown at the bottom of the upper cavity.

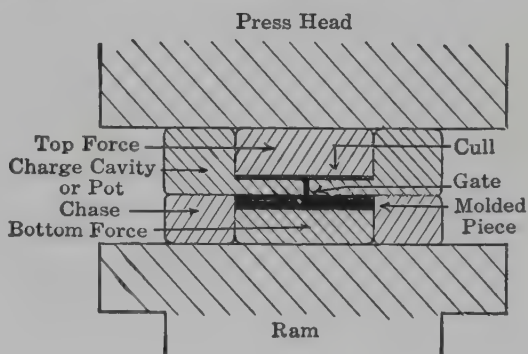


FIG. 7.7. In transfer molding thermosetting plastics, the required amount of material is placed in the upper cavity. Heat and pressure force material into lower cavity. (Plastics Catalog, p. 290, 1942 edition, published by Plastics Catalog Corporation.)

Molding Powder.—The actual materials used in any one of the molding methods discussed are rarely the basic plastics alone. In practice it is desirable to add various *compounding* agents in order to:

1. Insure good molding properties.
2. Extend the resin base and thus lower the cost of the product.
3. Modify the physical properties.

The mixture of components which results from the compounding procedure is recognized as the *molding powder*. There are numerous

types obtainable from the same resin base by the addition of different compounding agents. The choice of the most desirable molding powder for a particular use depends upon the property requirements of the fabricated piece.

Although the possibilities of formulation are numberless, a typical molding powder formula may be represented as follows:

Basic Resin, 40–90%. When thermosetting resins are used only 40–50% of the basic resin is necessary, while in the case of thermoplastic resins as much as 80–90% of the basic resin may be used. Only in rare cases is more than 90% of the basic resin employed.

Filler, 35–50%. Material such as wood flour, macerated fabric, mica, or asbestos is added for the purposes of extending the resin and modifying the properties of the finished product.

Plasticizer, 5%. When used with thermosetting resins, plasticizers are particularly valuable for aiding flow into the mold. When compounded (usually in higher proportions 15–35%) with the thermoplastics valuable characteristics of flexibility, resiliency, and ductility result. Typical plasticizers are dibutyl phthalate, tricresyl phosphate, and other high-boiling organic liquids.

Lubricant, 1%. This modifying agent is added particularly to prevent sticking to the mold surface. Typical lubricants are stearic acid, stearates, and beeswax.

Pigment or Dye, 1%.

Such a formulation should not be accepted too literally. Other ingredients may be added, some may be omitted, or the amounts applied may be varied above or below the limits indicated. Each change, of course, results in an alteration of properties and of behavior during processing. The most desirable formula for a particular requirement can be determined only after considerable experimentation.

Cold Molding.—The process of cold molding is one carried out by primary shaping of the resinous material by pressure alone. This, in turn, is followed by a heating procedure to insure complete filling of the mold, elimination of porosity, and curing (when thermosetting). The method is particularly applicable for asphalts and bitumens.

Casting.—The operation of *casting* is, as the name implies, simply one of pouring a liquid into a previously-formed mold (illustrated in Figure 7.8) followed by hardening of the liquid by a period of heating. It may be considered, therefore, as a molding process carried out without the application of pressure. The actual hardening process is lengthy and dependent upon such factors as temperature employed, catalyst present, and type of resin used.

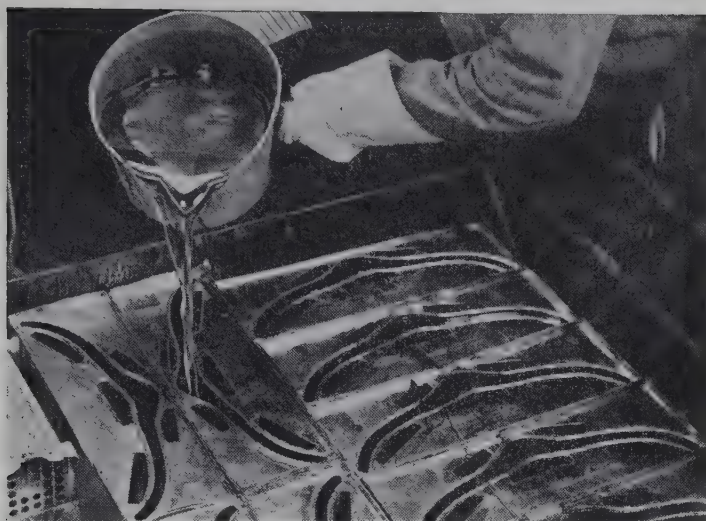


FIG. 7.8. Pouring liquid phenolic resins into previously prepared lead coat hanger molds. (Courtesy of Catalin Corporation.)

Laminating.—A plastics application which is now rivaling that of molding for general application is *laminating*. Basically, the operation consists of impregnating paper, cloth, or wood veneer with a resin varnish; drying, forming the cut, impregnated forms into the correct shape, and hardening by the application of heat and pressure. Actually, therefore, the process consists of bonding together layers of reinforced resinous matter. The bonding is accompanied by curing the resin applied during impregnation when a thermosetting type is used. Thermoplastics are rarely encountered in large-scale laminating operations. The various steps in the laminating procedure are illustrated in Figure 7.9 as impregnation in a dip tank (A), drying of the sheet stock (B), cutting the sheet to desired size (C), and curing the assembly by heat and pressure (D).

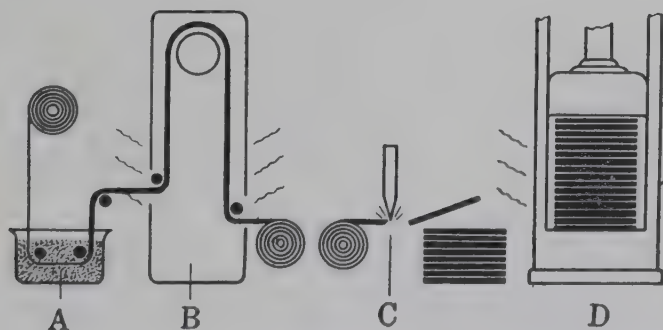


FIG. 7.9. Laminating. (Courtesy of Monsanto Chemical Co.)

A related process is that of *bonding*. In the plastics industry, for example, the terms “laminated plywood” and “bonded plywood”

are used in discussing the same product. Similarly, one may refer to the construction of an abrasive wheel, in which the abrasive is held by a resin binder, as a *bonding* process. Thus, although the term of bonding roughly pertains to much the same type of procedure as laminating, the essential difference is lack of impregnation in bonding as compared to its significant importance in the laminating procedure. In the latter, therefore, a more intimate comingling of the constituent parts results.

Coatings.—The use of resins in coatings is one of the oldest examples of their application. The value of both natural and synthetic types in lacquers useful for decorative or protective purposes has been well established. The general types of coating solutions include:

1. A simple resin solution which dries by evaporation of the solvent. This rapid-drying type may be composed of plastics variously compounded with plasticizers, pigments, and waxes.
2. Solutions in which the solute is a mixture of the resin with a drying oil. Drying in this case, occurs as a result of the combined polymerization and oxidation of the oil as the film becomes exposed by loss of solvent.

Adhesives.—Many and varied are the “resin glues” prepared for bonding together similar or dissimilar surfaces. The types of industrially applicable adhesives range from dilute, free-flowing solutions to hot-melt or heat-softenable solids. The value of each, however, is its ability to adhere strongly to one or more surfaces.

Summary.—The general terms in which the basic factors of the plastics industry have been discussed lead to the following conclusions:

1. The value of synthetic plastics is due to their inherent properties.
2. The variation of most desirable characteristics necessitates a choice of the most suitable type for particular requirements.
3. The final properties may be altered by either the compounding used or the method of fabrication applied.
4. An ideal plastic may be generally defined as one possessing properties of:
 - (a) Heat, chemical, and electrical resistance.
 - (b) Lack of plastic deformation or “permanent set.”
 - (c) Colorlessness and colorability.
 - (d) High tensile, compressive, flexural, and impact strengths.
 - (e) Adaptability to processing methods.
 - (f) Low cost and ready availability.

Review Questions

1. What are the general characteristics of plastics which make them valuable?
2. Why are so many types of plastics necessary?
3. Describe the essential steps involved in (a) compression molding, (b) injection molding, (c) extrusion, (d) transfer molding, (e) laminating, (f) casting.
4. Which of the above processes are generally used with
 - (a) thermosetting materials
 - (b) thermoplastic materials.
5. List four different types of materials that may be added to the base resin in making a molding powder and discuss the functions of each.

CHAPTER VIII

NATURAL PRODUCTS I: RUBBER

Although the inclusion of rubber and related materials in a discussion of plastic substances may be disputed, the similarity between its fabricating methods and those used with better-defined plastics is a sufficient basis for the inclusion. Mention of the word "rubber" immediately calls to mind certain features, such as elasticity and resiliency, by which the rubber state is recognized. It is the natural product which sets the standards by which synthetic products are judged. Therefore, it is only by a study of this product that an understanding of the related synthetic elastomers may be obtained.

Latex.—Latex is the name given to the milky fluid which is obtained from the rubber tree (*Hevea Brasiliensis*). The latex is not the sap of the tree, but is found in capillary vessels in the tree, and is obtained by cutting the trunk of the tree so that the latex-bearing canals are severed. A mature tree will yield about five grams of rubber per day or about four pounds of rubber per year. Latex has a specific gravity of 0.98 and consists of a colloidal dispersion of spherical or pear-shaped particles of caoutchouc in an aqueous suspension. The approximate composition of latex is given in Table I-8. Since the word rubber is so widely used for the finished product,

TABLE I-8. APPROXIMATE COMPOSITION OF LATEX ^a

Water	60%	Stearin, fats, soaps	1%
Rubber hydrocarbons	35%	Quebrachitol	1%
Proteins	2%	Inorganic constituents	0.4%

^a Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 173, Interscience Publishers, Inc., New York, 1942.

the word caoutchouc is frequently used to represent the pure hydrocarbon found in latex. The diameter of the caoutchouc particles varies from 0.5μ to 3.0μ . The caoutchouc content of natural latex is approximately 35% of the total weight. In order to prevent bacterial action and subsequent coagulation during storage and transportation, ammonia or borax is added to the latex.

Coagulation of Latex.—The colloidal latex solution can be coagulated by the addition of electrolytes. Those most commonly used are acetic acid and formic acid. When salts are used to coagulate latex, it has been found that a bivalent cation is more effective than a monovalent cation and less effective than a trivalent cation. These data indicate that the colloidal caoutchouc particle possesses a negative charge.

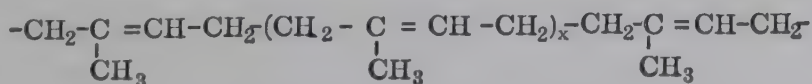
Further study has shown that the stability of the colloidal particles toward coagulating agents depends upon the pH value of the solution. Maximum stability exists above a pH value of 7 and below a pH of 3. Between these two values and particularly at a pH of 4–4.5, the colloidal particles are very susceptible to coagulation. These observations suggest that each colloidal caoutchouc particle is surrounded by a layer of a protective colloid which is amphoteric and has an isoelectric point (pH value of colloidal solution at which maximum precipitation occurs) of 4–4.5. Since proteins are amphoteric and have isoelectric points in the range of pH 4–5, it is reasonable to believe that the protective colloid is a protein adsorbed on the surface of the caoutchouc particle.

After deposition, the coagulated caoutchouc is forced between masticating rollers and washed thoroughly with water in order to remove all water-soluble impurities. If it is then dried simply by exposure to air, a *white crepe* rubber stock is obtained. To obtain *smoked sheet* stock, the washed product is dried at a temperature of 40–50° C. in an atmosphere of smoke produced from such materials as cocoanut shells or green wood. A uniform, dark color is characteristic of the smoked sheet.

Structure.—Analysis of the solid caoutchouc obtained from the coagulation of latex shows that it consists principally of the rubber hydrocarbon, approximately 3% of protein, 1–3% of resinous matter and less than 1% of ash. As a result of considerable experimental work, the rubber hydrocarbon has been identified as a linear polymer composed of units of isoprene, $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$. The linear



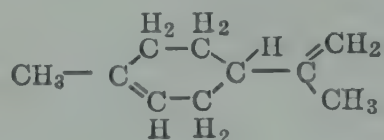
polymer may be represented as follows:



The essential steps involved in the proof of this formula are as follows:

1. Quantitative estimation of the elements shows the empirical formula to be C_5H_8 .

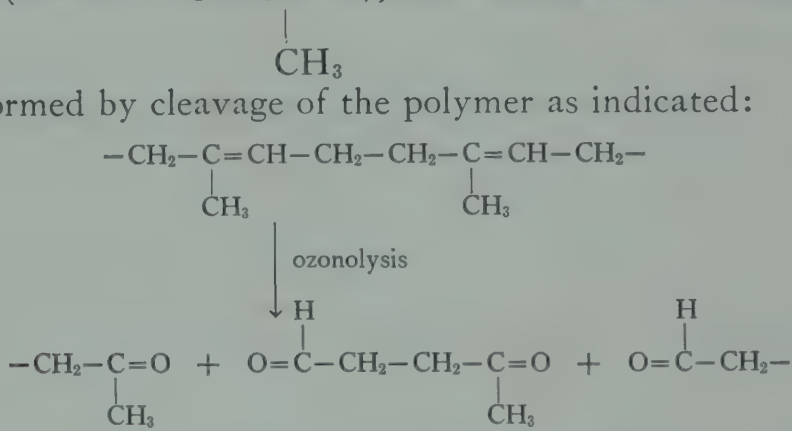
2. Destructive distillation of rubber produces isoprene or simple polymers of isoprene such as dipentene,



3. Saturation with bromine or iodine produces a compound having the empirical formula $C_5H_8X_2$. The existence of one double bond in each isoprene unit is thus shown.

4. Monomeric isoprene polymerizes to form a polymer having rubber-like characteristics. However, no polymer of isoprene has yet been synthesized that approaches rubber in usefulness.

5. Breakdown by ozonolysis causes the formation of levulinic aldehyde ($O=CHCH_2CH_2C=O$), or levulinic acid. Levulinic aldehyde is formed by cleavage of the polymer as indicated:



Levulinic acid may be formed by oxidation of the aldehyde by the hydrogen peroxide formed in the last step of the ozonolysis reaction.

6. The molecular weight has been variously determined as ranging between 100,000 and 300,000.

The determination of the arrangement of such macrochains in the structure of rubber is the result of observation of behavior under varied conditions and correlation of such data with those of other amorphous bodies. For example, when rubber is subjected to stress, the typical elastic behavior or recovery occurs until the elastic limit value is reached. Beyond this, the plastic flow which is only partially reversible and which results in a permanent set becomes typical. As the stress is increased the plastic flow continues until eventually the rubber breaks.

The effects of stress are also examined by subjecting rubber to a process known as *racking*. In this operation, the sample strip is heated, then stretched rapidly and finally cooled while still under maximum stress. An x-ray diagram of racked rubber is shown in Figure 8.1. The increase in kinetic energy of the polymeric chains permits release of the stresses involved and greater ease of mobility of the chains relative to one another. Then when the stressing load is released, only partial recovery from the stretched condition results. The processes of heating, elongation, cooling, and release of stress may be repeated several times until a permanent elongation of as much as 100-fold is produced. The sample is then spoken of as having been *racked*.

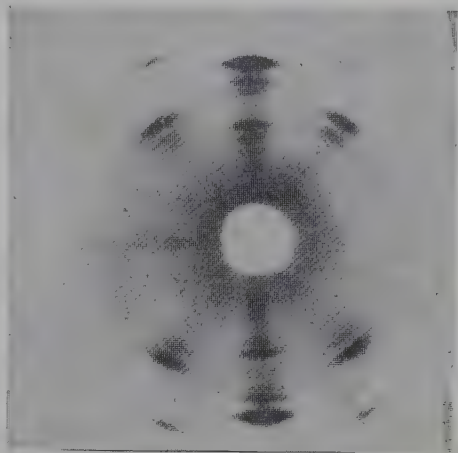


FIG. 8.1. X-ray diagram of "racked" rubber, showing only interference spots. The amorphous band has entirely disappeared. (Courtesy of Ernst A. Hauser, Massachusetts Institute of Technology.)

The third phenomenon of interest in the examination of stretched rubber is the typical x-ray diagram obtained from it. Ordinarily, when not under stress, rubber, at room temperature, shows the typical x-ray diagram of amorphous bodies. When stretched, however, a regular fiber arrangement is indicated by x-ray patterns. Typical x-ray diagrams of both states are shown on p. 14.

These facts indicate that rubber consists of hydrocarbon chains existing in coiled, irregular forms. Existence of at least a portion of the molecules in a crystalline state, however, is shown by intensified rings in the x-ray diagram of frozen rubber. When rubber is cooled, the kinetic energy of the molecules is decreased to a point which permits the chains to remain in an oriented position relative to one another. The x-ray diagram of "frozen rubber" is shown in Figure 6.4, p. 103. Proof of the existence of these crystalline regions in rubber indicates that the stretching of rubber does not produce the crystalline area, but merely causes orientation of the existing crystallites. The first elongation, when rubber is stretched, is simply one of uncoiling or straightening of the spiraled chains into a regular arrangement, as illustrated in Figure 8.2. During this stage, the property of elasticity is retained and a crystalline pattern results. When the extreme has been reached, however, elongation must be by the slow movement

or slipping of chains relative to one another. Ordinarily such movement results in permanent set or, when aided by release of strain by heat, as in racking, a permanent elongation is produced. Much of the actual configuration of the polymeric chains may be clarified by a discussion of elasticity.

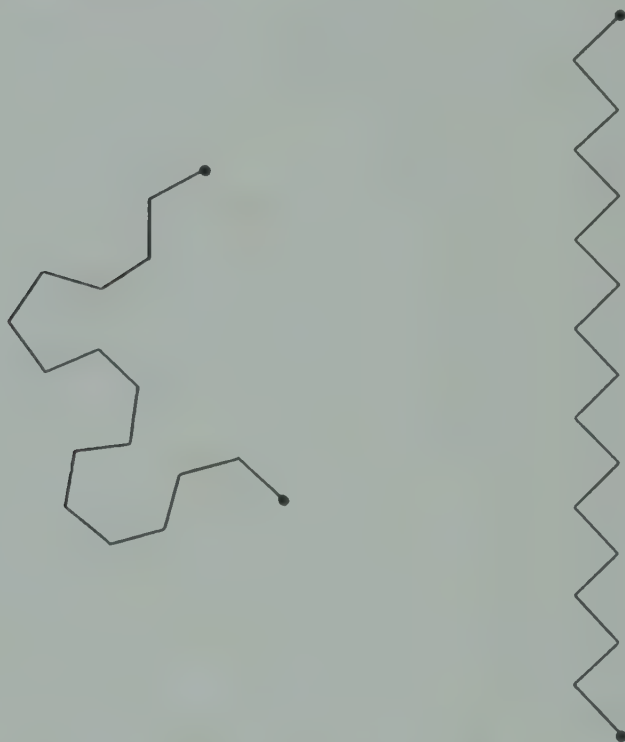
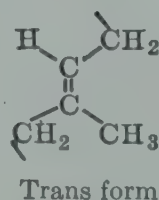
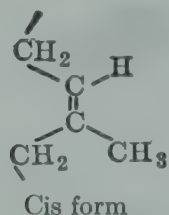


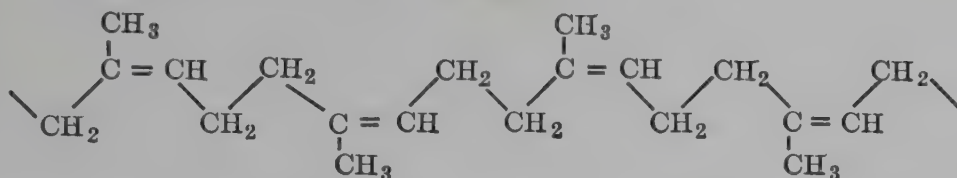
FIG. 8.2. Configurations of a chain molecule. (Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 158, Interscience Publishers, Inc., New York, 1942.)

Elasticity.—The relationship between structure and the property of elasticity is not definitely known. However, it is worthwhile to discuss some factors which may be pertinent to this relationship. From the standpoint of stereochemistry, the possibility of the existence of two distinct stereoisomeric polymers composed of isoprene units may be illustrated by the following formulas:



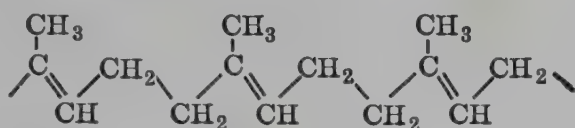
Evidence has been obtained to indicate that the following cis con-

figuration is present in rubber molecules:



The evidence is found in x-ray diagrams which show that the *identity period* along the chain consists of two basic isoprene units. Observation of the formula given above shows that identical positions along the chain are separated by two monomeric units.

The *trans* configuration, on the other hand, occurs in the polymeric chain of gutta percha:

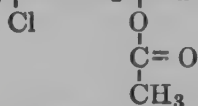


This formula is based upon the x-ray data showing that the *identity period* consists of one basic unit.

The two stereoisomers, therefore, represent different polymeric materials possessing different and specific properties. The characteristic of elasticity is shown by both rubber and gutta percha. Rubber, however, has a much greater elasticity than gutta percha. From this it may be concluded that no one physical configuration and no particular grouping of specific atoms is responsible for such properties. Thus, the category of rubber-like solids includes such dissimilar materials as polyvinyl alcohol, $(\text{CH}_2\text{CH})_n$,



vinyl chloride-acetate copolymers, $(\text{CH}_2\text{CH}-\text{CH}_2\text{CH})_n$,



polychlorobutadiene, $(\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2)_n$, etc.



There is no definite rule relating chemical structure to rubber-like properties. However, the tendency of many amorphous materials to exhibit rubber-like characteristics indicates that the amorphous state is a primary requirement.

A consideration of the molecular arrangements found in stretched and unstretched rubber is also of value in attempting to find an explanation for the property of elasticity. Unstretched rubber

produces an x-ray pattern characteristic of an amorphous solid. As the rubber is stretched, there is a gradual change in the x-ray pattern toward the intensified spot pattern characteristic of a crystalline arrangement of the molecules. As described on p. 129 the first stretching is believed to cause a straightening out of the kinked molecules. As the stretching proceeds, the crystallites which are believed to be present in rubber, though detected only in frozen or stretched rubber, gradually become oriented in a regular crystalline pattern, with the chains lying parallel to each other in the direction of the application of the stress. The elastic limit is reached near the end of the second portion of the stress-elongation curve represented in Figure 6.3 on p. 102. Evidence for the existence of a parallel arrangement of the molecular chains is found in the fact that when rubber in a stretched, crystalline state is frozen and the brittle solid is smashed, well-defined fibers are obtained. (See p. 39.)

It should be pointed out that even under maximum stress, it is probable that some of the molecules exist in an amorphous, non-crystalline state. Hence, rubber under varying amounts of stress exists partly in the amorphous state and partly in the crystalline state. Temperature, age, and previous treatment of the rubber are also factors affecting the proportions of amorphous and crystalline material present in any given sample of rubber. While the application of stress tends to increase the proportion of rubber which exists in a well-oriented crystalline state, thermal agitation and the undirected internal energy of the molecules tend to decrease the extent of the crystalline arrangement. As soon as the stress is removed, the factors of thermal agitation and internal energy exert their maximum effect and the molecules return to their normal state in which only a low order of crystallinity exists. This change is, of course, accompanied by a contraction of the rubber to its original dimensions.

The characteristic of elasticity must be related to the ability of certain molecular chains to move from and revert to their original coiled, amorphous positions. One theory offered to explain this movement is that the rubber-like state is actually intermediate between that of a liquid and that of a solid. In one dimension a group of atoms is held by linkages associated with solids and is characterized by the high viscosity, $\eta > 10^9$ c.g.s., of solids. In the other two directions the binding forces associated with liquids and their viscous properties ($\eta < 10^7$ c.g.s.) are responsible for behavior characteristics. When stretched, proper alignment of the molecules results if the internal friction between chains is not higher than

$\eta = 10^7$. When the friction is above this value an unextensible amorphous solid results. If the internal friction is high, as in polyvinyl acetate or polystyrene, it must be reduced by artificial means such as heating or introduction of a swelling agent, i.e. plasticizer, before rubber-like extensibility can occur. On the other hand, it is possible to start with a polymer such as polyvinyl chloride which exists in a partially crystalline state. In this case the high value of η is due to the more or less orderly arrangement of the polar molecules. By the addition of suitable plasticizing agents the orientation of the polymer molecules is destroyed, with the production of an amorphous structure possessing a low internal friction. This plasticized polyvinyl chloride exhibits the rubber-like property of extensibility.

When all factors are summarized, however, it is obvious that stretching may occur in any of the polymeric types mentioned when conditions of heat or plasticization are properly regulated.

Correlation of internal friction with movement of the molecules may be extended to include the solid dimension. When the internal friction in this dimension is decreased to a value of $\eta = 9$ c.g.s., slipping of the molecules past one another results. The result is plastic flow rather than elastic deformation.

Relaxation.—The rôle of plastic flow and its resultant effect of permanent deformation has been mentioned previously (p. 66) in discussions of stress-strain behavior of plastics. When the stress applied to many rubber and rubber-like plastics is maintained at a constant value, the deformation continuously increases and, in consequence, the tension on the test strip actually diminishes. X-ray study has shown that the oriented chains may move relative to one another. Lack of high binding forces and the presence of thermal agitation are responsible for this *relaxation effect*, i.e., relaxation of tension due to slow movement of the molecules.

Crystallization is opposite to relaxation in that it involves orientation of the molecules, but crystallization is similar to relaxation in that it causes a decrease in tension on the plastic strip. Increased crystallization causes a decrease in the relaxation effect because the plastic properties are decreased. Unvulcanized rubber has been shown to flow less when subjected to large loads than when subjected to small loads. This observation results from the fact that higher loads cause crystallization and prevention of flow.

A discussion of the factors involved in the plastic flow responsible for relaxation and of the elastic after-effect and creeping which may occur when the deforming tension is released, is concerned primarily with the physical structure of the macromolecule. It is found that

the resistance to flow of the plastics molecules past one another is several times higher than the resistance involved during elastic deformation. Also, the molecular weight of the plastic is of fundamental importance. Materials of low molecular weight have a high flow, large relaxation and, therefore, possess a high *plasticity*. In addition, the configuration of the molecules has a direct effect. The relaxation periods of varying rubber materials differ, for example, because of variations in pre-treatment (mastication), temperature, loading, and degree of vulcanization. The latter property is responsible for differences in the amount of cross-linkage present. (See p. 143.) When flow is restricted by a portion of the structure existing in the cross-linked form, the relaxation period is limited. The relaxation then causes a rapid decrease in tension followed by a very slow or negligible decrease. The product exhibits limited relaxation. During the relaxation period, the portions not bound into a network structure are capable of movement, but limitation of the tension decrease is involved because sufficient stress must remain to maintain the cross-linked parts in an oriented parallel arrangement. When tension is completely released, the parallel arrangement is lost and the free-flowing molecules become compressed in a direction perpendicular to the direction of stress application by the relaxed net-work system. Elastic after-effect and creep then result as the compressed molecules move to diminish the compressing force. Slow recovery of deformation is the visible effect of the creeping.

The behavior of rubber-like substances when subjected to stress is summarized by plasticity measurements. Fundamentally, the plastic behavior is being studied. Plastometers designed to measure plastic characteristics are based upon the same principle. Deformation by a known force, for a given period of time and at a controlled temperature, permits observation of relaxation and recovery behavior.

The plastometer curve (Figure 8.3) shows the changes which accompany the application and release of a compressive force upon a plug of the rubber being tested. The first change, pictured in the graph between numbers 1 and 2, is a rapid reduction in the height of the plug. Pictorially, the change is represented by the accompanying drawings which show the plug before the application of pressure (No. 1) and after the initial rapid change (No. 2). The second stage of the deformation is due to the slow plastic flow which occurs over a long period of time and is completed at the position on the graph designated as number 3 and diagrammatically by number 3. When the loading is removed, the initial, rapid, elastic recovery shown between positions 3 and 4 is followed by a slower recovery,

from 4 to 5, which is commonly termed "elastic after-effect." The plug, however, does not return to its original height and the permanent deformation is the difference between the original height at 1 and the final height at 5.

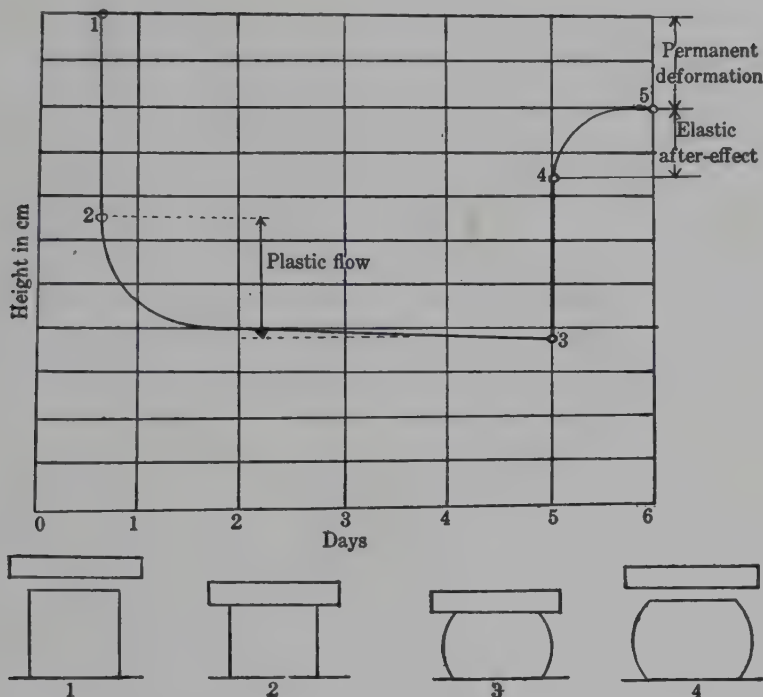


FIG. 8.3. Plastometer curve for perbunan. (Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 172, Interscience Publishers, Inc., New York, 1942.)

Hysteresis Effect.—The peculiar effect and importance of *hysteresis loss* in the explanation of observed phenomena of rubber may be illustrated by correlating molecular displacement with the results of temperature changes on the rebound figures. When a rubber ball is dropped, the height to which the ball will return is found to vary strangely with the temperature. The approximate values are given in Table II-8. In all cases the percentage of recovery is actually representative of the amount of energy available for rebound. Any large distortion of rubber (or other plastic types) involves movement of molecules relative to one another. In turn, the molecular movement causes a loss in kinetic energy because a portion of the energy ordinarily available is used up by the intermolecular friction. Also, it has been found that the amount of friction generated is directly proportional to the strength of the molecular attractions which exist.

TABLE II-8 ^a

Temp.	Rebound
100° C.	83%
20° C.	77%
- 20° C.	24%
- 40° C.	4%
-100° C.	70%

^a Data taken from Lewis, Squires, and Broughton, *Industrial Chemistry of Colloidal and Amorphous Materials*, p. 422. Reprinted by permission of The Macmillan Company.

Thus, the decreasing values of rebound at -20°C . and -40°C . illustrate the fact that the molecular attractions are increasing as the temperature is lowered. Decreased thermal agitation permits stronger intermolecular bonding forces. The ultimate is reached at -40°C ., for at this temperature practically all the kinetic energy is consumed in overcoming the attractions. Strangely, at -100°C . the rebound is again great, but this is explained by picturing the molecules in permanently fixed positions. The attractive forces are so high in this case that no ordinary distorting effect may overcome them, therefore there is no loss of energy due to friction.

The value of *hysteresis* loss is representative of energy used in overcoming the internal friction. In other words the mechanical energy supplied to a system capable of showing hysteresis effect is

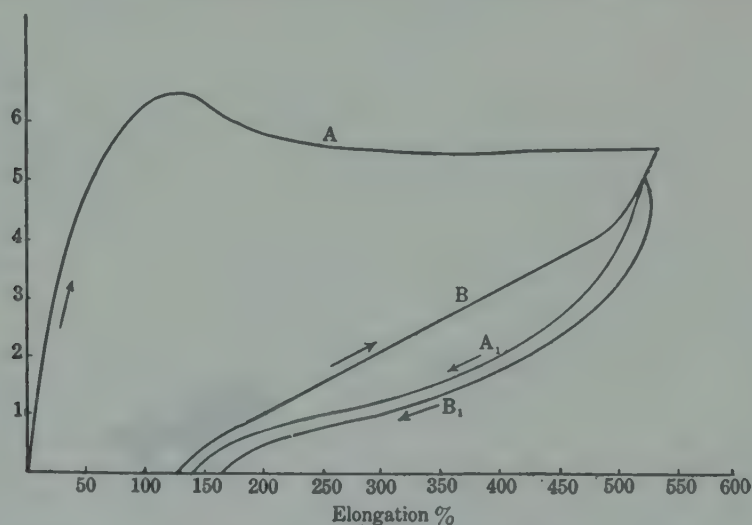


FIG 8.4. Hysteresis loops for raw rubber. AA_1 : First cycle of extension and retraction. BB_1 : Second cycle. (Davis and Blake, *Chemistry and Technology of Rubber*, p. 68, Reinhold Publishing Corp., 1937.)

never completely recovered. The effect is graphically illustrated in Figure 8.4. The amount of energy involved in hysteresis loss is represented by the difference between energy put into the system and that recovered. The energy lost in the first cycle of extension and retraction is represented by the area within the curves AA_1 (area under curve A minus area under curve A_1). The energy lost in the second cycle is represented by the area within the curves BB_1 . The difference is dissipated by its conversion into heat. Actual hysteresis effects involved in natural rubber have proved difficult to duplicate or approach in synthetic types.

Methods of Industrial Application.—Commercially important rubber products can be obtained either from solid stock (pale crêpe or smoked sheet) or from latex. The solid stock is generally used for the preparation of articles where the rubber layer is reasonably thick, while latex is particularly desirable for dipping or coating operations where a thin film of rubber is desired.

SOLID STOCK

Milling.—The first operation carried out in the utilization of crêpe or smoked sheet involves the physical plasticization of the solid stock. This process is known as the "breakdown."

Actually, the process consists in subjecting the rubber to a severe mechanical shearing stress. Under such conditions the rubber gradually becomes softer and more readily deformable. Mechanically the change may be produced by use of either a *rubber mill* (Figure 8.5) or a Banbury mixer. The former consists of two horizontal steel rolls. These rolls move toward one another in a clockwise-counter-clockwise movement at speeds regulated by enmeshed gears driven by electric power. The speeds of the rolls usually differ about 25% between the faster-moving back roll (furthest from operator) and the slower-moving front roll. Also, the opening between the rolls may be adjusted to accommodate different milling procedures or various sized batches. The shearing force is produced by first banding the rubber batch on the front roll and adjusting the mill opening so as to maintain a bank of rubber in the upper hollow between the rolls.

By continually cutting and folding the rolling sheet of stock, a uniform plastic mass can be obtained. The temperature of milling may be regulated by internal cooling or heating of the rolls. Thus, under set conditions of batch size, mill opening, temperature, and time of operation, results can be obtained which are easily duplicated.

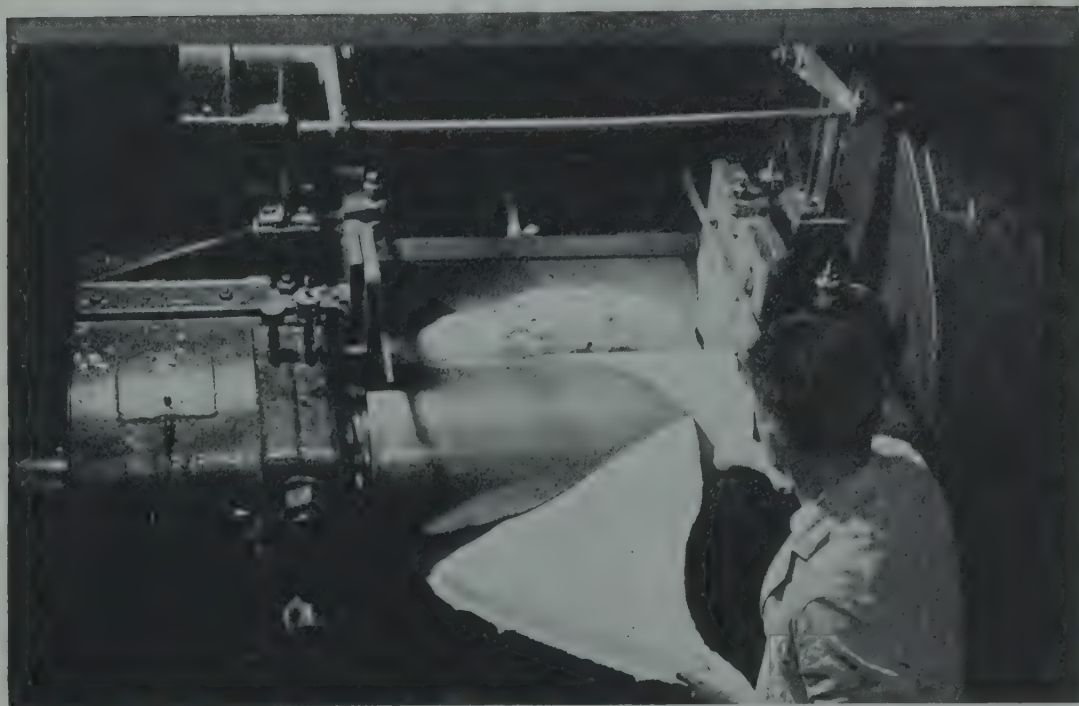


FIG. 8.5. Experimental size rubber mill. (Courtesy of The Resinous Products and Chemical Company.)

In general, milling is done at temperatures below 70°C . for twenty minutes.

The Banbury mixer consists of a water-jacketed chamber equipped with rotating arms. The walls of the mixing chamber are concentric to the arms, which rotate at different speeds. Under these conditions, a continual shearing action results. Again the controllable factors of temperature and time of operation regulate the degree of breakdown caused. More careful adjustment of conditions is necessary, in this case, however, because of the fact that breakdown proceeds so much more rapidly than with the rubber mill. A diagram of the Banbury mixer showing the movement of the rotors is shown in Figure 8.6.

The actual structural effects produced during the breakdown period may be postulated from a consideration of the properties of the product. A milled sample of rubber has an increased degree of plasticity, greater ease of solvation and lower viscosity in solution, when compared with an untreated sample. These facts point immediately to a reduced chain length. Further, it has been determined that the maximum speeds of breakdown occur at temperatures below 70°C . or above 160°C . The theoretical explanation of these effects is that a chemical oxidation occurs under the influence of

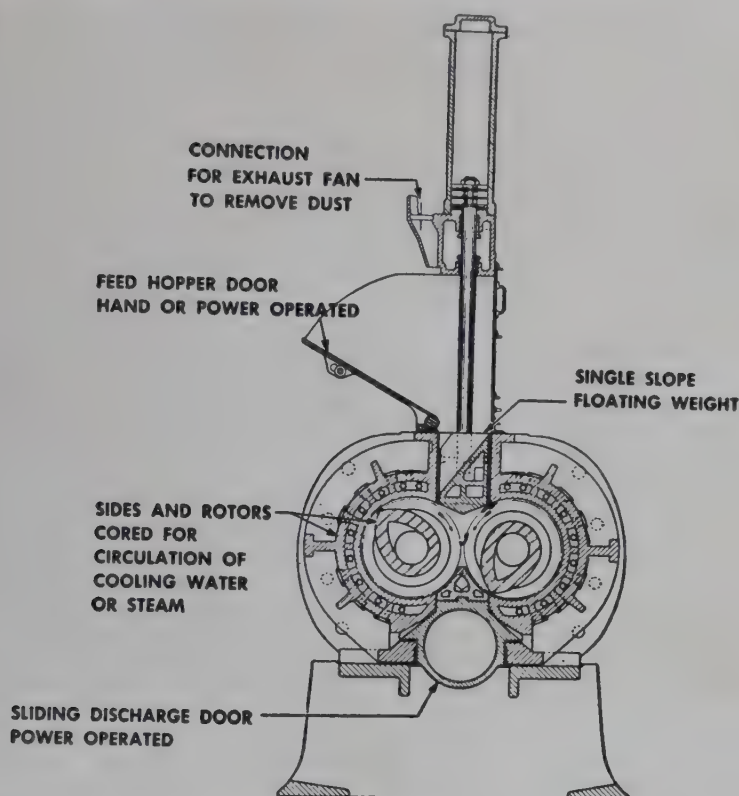


FIG. 8.6. Diagram of Banbury mixer. (Courtesy of Farrel-Birmingham Co., Inc.)

mechanical stress. The reaction is assumed to involve both oxidation and cleavage of the rubber molecule at positions of unsaturation:



The relation between speed of milling and temperature is explained by the following factors. Below 70° C., mechanical stress is sufficient to cause the reaction; above this temperature, however, mechanical stress diminishes and the speed does not again reach a maximum until the temperature of 160° C. is reached. At this point the driving force of the chemical change is heat. The reaction may proceed even in the absence of mechanical stress.

Some experimental support for the explanation proposed is provided by the following facts:

1. There is no breakdown of rubber when it is milled in an inert atmosphere of nitrogen.

2. No appreciable breakdown occurs by milling polyisobutylene because of the absence of unsaturation in the compound.

Compounding.—The second stage of solid rubber processing is *compounding*. Both the rubber mill and the Banbury mixer can be used for the addition of various materials to the rubber. These compounding agents are added to (1) extend the rubber, (2) impart certain desirable properties to the product, (3) effect a cure of the rubber compound. The more important compounding agents and their functions will be discussed.

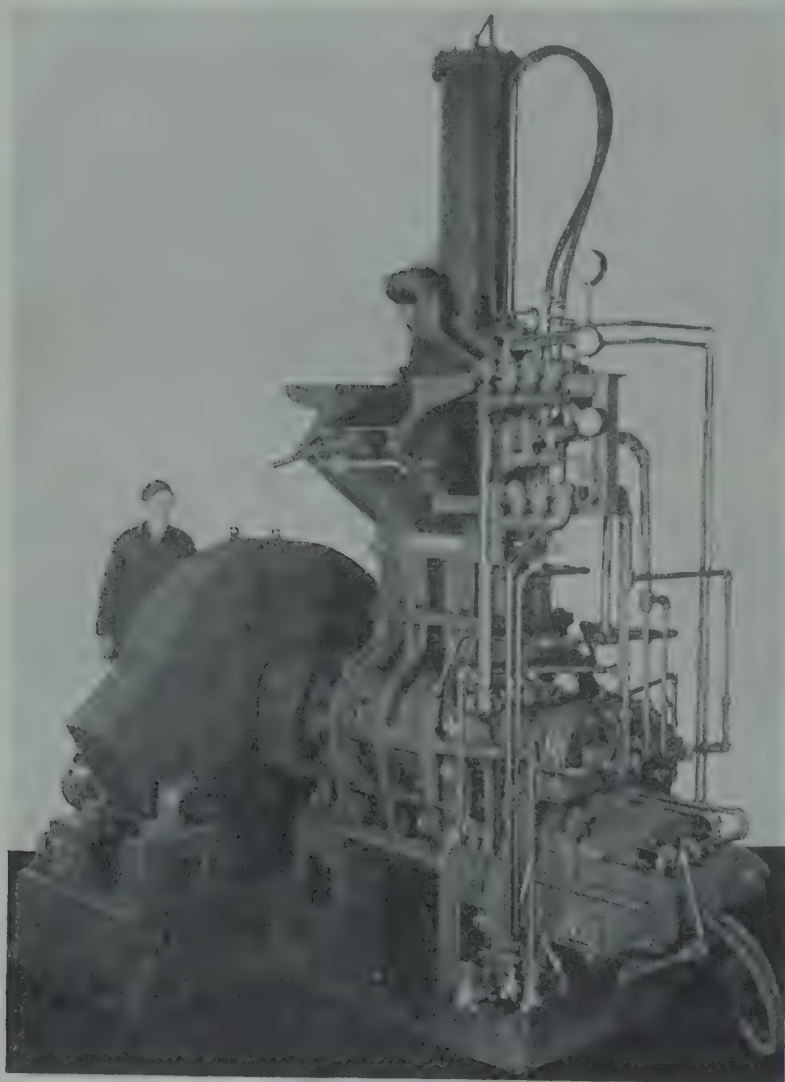


FIG. 8.7. Banbury mixer used for processing plastics and rubbers.
(Courtesy of Farrel-Birmingham Co., Inc.)

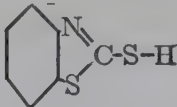
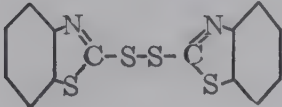
1. *Fillers and Reinforcing Agents.* These are useful for the same reasons used to explain the addition of fillers to molding powders. Such materials as carbon blacks and magnesium carbonate (rein-

forcing agents) extend or dilute the rubber. More important, however, is the fact that they enhance the characteristics of tensile strength, modulus of elasticity, and abrasion resistance. Other materials such as limestone or talc (fillers) act only as diluents.

2. *Softeners*. A liquid or soft-resinous type of plasticizer is also used in rubber compounding to aid the further processing or to alter the physical properties obtained after vulcanization. Low moduli of elasticity and higher elongations, for example, are produced by the inclusion of such materials as pine tars or rosin oils.

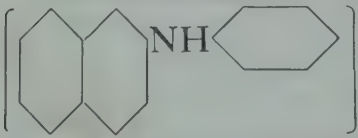
3. *Accelerators*. Numerous chemicals, which differ widely in structure, are included in the compounding of rubber in order to catalyze the actual vulcanization process. They are known as *accelerators*. By their use, the percentage of sulfur required for vulcanization has been considerably reduced (from 8% to 1.5–2%). The accelerators enable the vulcanization or “cure” to be completed in a shorter time and at a lower temperature. The names and formulas of a few typical accelerators are given in Table III–8. In general, they are nitrogen or sulfur containing compounds which may exert their particular effect by first forming an intermediate compound with sulfur. This intermediate may decompose with the

Table III
Typical Accelerators

Compound	Formula
Diphenylguanidine	$(\text{C}_6\text{H}_5\text{NH})_2 \text{C}=\text{NH}$
Tetraethyl thiuram disulfide	$ \begin{array}{c} (\text{C}_2\text{H}_5)_2\text{N}-\text{C}=\text{S} \\ \\ \text{S}-\text{S} \\ \\ (\text{C}_2\text{H}_5)_2\text{N}-\text{C}=\text{S} \end{array} $
Tetramethyl thiuram disulfide	$ \begin{array}{c} (\text{CH}_3)_2\text{N}-\text{C}=\text{S} \\ \\ \text{S}-\text{S} \\ \\ (\text{CH}_3)_2\text{N}-\text{C}=\text{S} \end{array} $
Mercaptobenzothiazole	
Butyraldehyde aniline	$\text{C}_3\text{H}_7\text{CH}=\text{NC}_6\text{H}_5$
Benzothiazyl disulfide	

liberation of sulfur in an active or exceptionally finely subdivided form for reaction with the rubber hydrocarbon.

Accelerators may be classified as *ultra*, *rapid*, or *moderate*. The ultra accelerators cause curing below 100° C. in a few minutes; the rapid accelerators require temperatures of 100–130° C. for 20–40 minutes while the moderate accelerators are active at 140–150° C. over a longer period. Inorganic secondary accelerators such as zinc oxide and litharge are often added to facilitate the vulcanization and to improve the tensile strength of the product.

4. *Antioxidants*. Materials such as phenyl- β -naphthylamine are  added in small percentages to reduce the deleterious effects of embrittlement caused by aging.

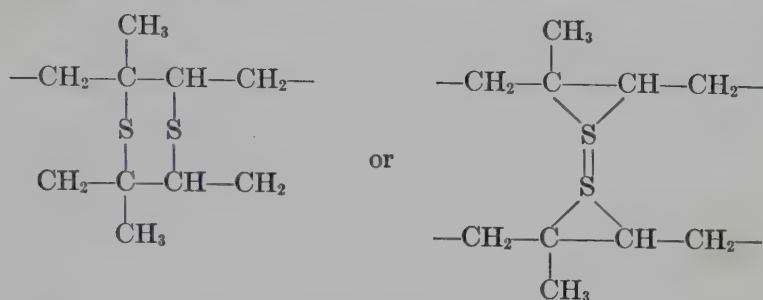
5. *Sulfur*. This is the most important substance added to the rubber for compounding. It is the agent which causes vulcanization, changing the rubber from a sticky, tacky mass to a strong and useful product.

In practice, rubber processing involves the incorporation of these compounding agents immediately after the breakdown period. Although the amounts and also the order of addition may vary, a typical procedure, giving both the amounts and the order in which the materials are added, is as follows:

Rubber	100 parts
Plasticizer	5 parts
Reinforcing agent	100–200 parts
Accelerator	1 part
Antioxidant	1 part
Zinc oxide	5 parts
Sulfur	2.5 parts

Sulfur is usually the last agent to be added in order to prevent partial curing, known as *scorching*, while the mixing operation is being carried out. Consequently, vulcanization is the final operation in the manufacturing of solid rubber. Fundamentally, the change is one by which rubber is converted from a linear (thermoplastic) substance to a cross-linked (thermoset) material by reaction with sulfur. The mechanical process involves the introduction of the heat-plasticized compounded rubber into mold forms, sheeting, or tubing by use of the proper forming device, followed by the application of heat to the mold for a regulated period of time.

The chemical nature of the change is pictured as an addition of the sulfur to the double linkages of rubber. Actually, it has been found that approximately 2% of the total amount of sulfur required to saturate the double bonds is necessary for a complete cure to the state of cross-linkage necessary for desirable physical properties. The irreversible nature of the chemical change and the great change in physical characteristics caused by a small amount of sulfur are believed to be the result of the formation of cross-linkages. These are formed by the interaction of the linear polymer molecules with sulfur. The cross-linkages may be represented as follows:



The plausibility of such an explanation is supported by the fact that increasing amounts of sulfur with an accompanying increase in the number of cross-linkages, cause a great increase in the hardness of the product. Further evidence to support the belief that sulfur adds to the double bonds is found in the fact that unsaturation of vulcanized rubber, as measured by the addition of halogens, is always less than that of unvulcanized rubber.

Under the usual procedure of heating at 140° C. for 45 minutes, the typical physical changes which may be expected as a result of vulcanization include: change of thermoplastic character to that of thermosetting, increase of tensile strength, decrease in permanent set, and decrease of solubility in the usual solvents.

Fabrication Techniques.—The methods applied to rubber compounds in order to produce vulcanized products follow various shaping operations to form the rubber into the proper dimensions. Such procedures as molding, tubing, extruding, calendering, and frictioning are typical of such processes. Molding of rubber compounds is similar to compression molding of general types of plastics. Pressure (500–2000 lbs. per sq. in.) and heat (115–170° C.) are applied simultaneously in order to shape the product until vulcanization is complete (10 minutes to several hours). Extrusion of a continuous strip or tube (tubing) is carried out in the customary extrusion equipment. The compound is fed by continuous rotation

of a helical screw through a heating chamber, which in turn, leads into a suitably designed orifice or die where the material is shaped into a tube or strip. The shaping step may be followed by a steam cure, dry heat cure, water cure, or lead press cure. When the object is to be steam cured, it is subjected to live steam at, usually 115–150° C. for variable periods of time (30 minutes to 24 hours). The product may be supported on pans or trays, placed on a mandrel, or wrapped by strips of wet fabric. Dry heat curing methods are comparable to those of steam except for the fact that the atmosphere with which the object is in contact is dry or moist air rather than steam. In water curing, the product, in either roll form or encased in fabric wrapping, is immersed in water. Pressure may be exerted on the water chamber up to 50 lbs. per sq. in. and the temperature can then be maintained as high as 125° C. Lead press cures are often applied in the vulcanization of continuous forms such as hose or cables. Molten lead is extruded on the surface of the rubber and curing is carried out in a steam chamber. The lead covering conducts the heat from the steam to the compound. A smoother surface and a denser product than those obtained by open steam cure may be produced.

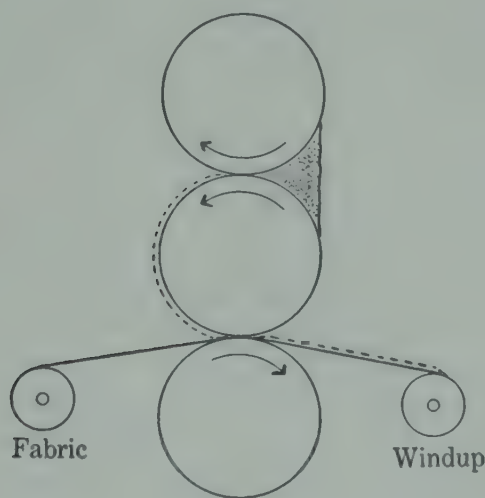


FIG. 8.8. Skim coating showing combined compound and fabric being wound.

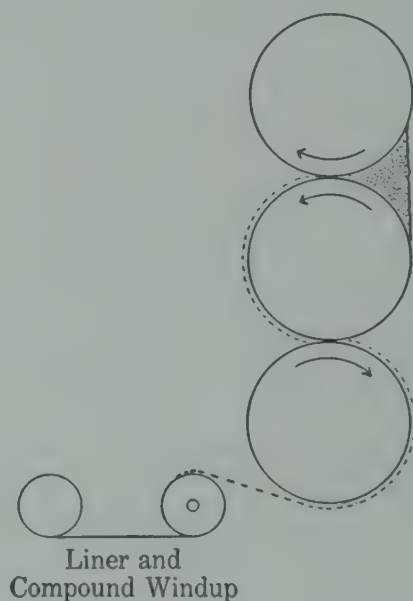


FIG. 8.9. Sheet calendering showing continuous film being wound with fabric interliner to prevent sticking of adjacent plies.

Calendering operations consist of processing the rubber compound into sheet form or combining it with fabric. There are three general types: sheet calendering, frictioning, and skim coating. All are applicable to other plastics. The equipment, i.e., calender, is of the general design pictured in Figures 8.8 and 8.9. The operation consists of first warming the compound and then placing it in the nip between the middle and top rolls. By proper regulation of the roll speeds and temperatures, the sheet formed between the rolls may be caught on the middle roll and then passed between the middle and bottom rolls. The film may be cooled and rolled if a sheet calendering is involved. In the case of frictioning or skim coating, however, a thin sheet of fabric is passed between the lower rolls with the rubber compound. When the compound is sufficiently plastic it may be squeezed into the pores of the fabric and a frictioned product is obtained. When the compound is merely combined with fabric without appreciable filling of the pores, the product is referred to as a skim-coated fabric.

LATEX

Industrial Methods of Utilizing Latex.—In addition to the method of compounding and vulcanizing rubber, as described above, latex can be used directly in the making of finished rubber goods. It is particularly valuable in many coating and dipping processes, e.g., in the making of thin rubber gloves for the use of surgeons and others.

The latex obtained from the rubber tree is stabilized at the plantation by the addition of ammonia or borax. This precaution is necessary in order to prevent the action of bacteria from causing coagulation. The latex may then be concentrated if a higher solids content is desired. There are three concentration processes in general use, namely, centrifuging, creaming, and evaporating. These processes are capable of raising the solids content of latex from about 30% to 50–70%.

1. *Centrifuging.* If the latex is subjected to centrifugal action similar to that employed in a cream separator, a dispersion can be obtained which contains approximately 60% of solids and is free from protein and resinous matter.

2. *Creaming.* The latex may be made to separate into two distinct layers by the addition of a small amount of a colloidal material having a high absorption capacity for water. Irish moss, locust bean gum, and gum tragacanth are typical colloids used. The creaming effect has been explained by Hauser and Dewey¹ as due

¹ Hauser and Dewey, *Ind. Eng. Chem.* 33, 127 (1941).

to the dehydrating action of the colloidal material on the protein constituents present as natural stabilizing agents in the latex. As a result of this dehydrating action, these protein stabilizing agents lose their effectiveness. This destabilization is followed by an agglomeration of latex particles and the separation of a top layer having a high concentration (50–60%) of solids. This process is known as Traube's process.

3. *Evaporating.* Simple evaporation after additional stabilization by a protective colloid results in concentration to a solid content of as high as 70%.

When the concentrated latex is used to make a rubber product, the ammonia preservative is first blown out of the latex by means of air. Compounding of the rubber latex is carried out by the addition of suitable agents in dispersed form to the latex. Although the effective agents are comparable to those used in compounding solid rubber, the addition of various dispersing and stabilizing agents is necessary. Thus, fillers, accelerators, sulfur, stabilizers, wetting agents, thickeners, and antioxidants are used. The compounding may be carried out by preliminary mixing and dispersing of the compounding agents in either a pebble mill or a colloid mill, or by the addition of each agent previously dispersed in water. A typical formulation may contain:

Latex	100 parts (calculated on basis of rubber content)
Filler	40 parts
Zinc oxide	3 parts
Accelerator	1 part
Antioxidant	1 part
Sulfur	1 part
Dispersing agent	.25 part
Stabilizing agent	.3 part

One of the most important industrial applications of latex is as an adhesive for use on surfaces which are ordinarily easily wetted by water. The adaptability of this adhesive to many shoe construction operations has brought about widespread acceptance in the shoe industry. In most cases a latex containing no curing agents is used with or without an added resin emulsion. The solids content of the latex may be varied, but latex containing 60% of solids is the material most widely used. Latex is also used as an adhesive for book-bindings, as a waterproofing agent for paper, and as a laminating material. In combination with bitumen, latex is often used as a

road surfacing material. The mixture of the two is produced by preliminary emulsification of the bitumen followed by suitable compounding.

Such articles as gloves, seamless overshoes, beach shoes, balloons, bathing caps, or moisture resistant containers may be readily produced from latex by a mechanical dipping process.² In this procedure a form, designed to the shape of the piece being manufactured, is dipped into the latex, removed, and dried. Repetition of this cycle of operations gradually results in the formation of a shaped film. The deposition of the film upon the designed form is dependent upon the viscosity of the latex, its concentration, the surface tension, and the speed of insertion and removal. Since most of the problems encountered in this process are concerned with the formation of a strong film with as few operations as possible, specialized methods for the development of this film have been devised. At the same time, precautions must be taken to form a smooth, even film rather than one containing bubbles or thickened regions. The deposition of the rubber particles from the latex may be accelerated by the use of suitable electrolytes deposited upon the form, use of a porous form with suction, or by coating each successive layer with an electrolyte. Vulcanization is accomplished by heating the dry rubber film which has been deposited on the form. A continuous rubber thread is now produced from latex by extruding the latex through tiny orifices into a coagulating bath of acetic acid or a concentrated solution of ammonium acetate. The resultant thread is caught up by conveyors, washed, dried, and vulcanized.

Rubber articles have also been manufactured from rubber latex by an electrodeposition procedure. Since the particles of solid rubber possess negative ionic charge, the rubber film may be deposited upon a metallic anode. If a rubber coating is desired, the piece to be coated may often be used as the anode, or if a shaped article is desired, the anode may be designed to the desired shape, the deposited rubber stripped from it after deposition and vulcanized by heating. In this process a rubber latex containing 35–40% solids is generally used and films of rubber having a thickness up to 1 cm. may be conveniently produced. Deposition of solid rubber from the latex is also encountered in *latex molding*. The technique in this process consists of casting the latex in the desired shape and allowing it to set or gel in the mold. The process is dependent upon the fact that the latex mixture can be gelled in a controllable period of time.

² P. Klein, *Trans. Inst. Rubber Ind.*, 9, 395 (1934).

The coagulation may be controlled by a number of methods. Most of these are dependent upon the use of electrolytic coagulants. When a small portion of calcium sulfate is added to the latex, for example, the latex will gel when heated. When ammonium persulphate is used as the coagulant, its effectiveness increases as the temperature is raised because its solubility is increased. By such a process a solid, firm coagulant of rubber-like quality but containing much of the water originally present may be produced.

Latex is often used, also, in appreciable quantities in the textile industry.³ Treatment of the fabric by an impregnation process results in improved flexibility, resistance to salt water, and better tailoring qualities. Such a technique is often used in producing belting, fishing nets, shoe soles, and beach coats. The desired degree of impregnation and adhesion is obtained by the use of wetting agents to decrease the surface tension and thus improve the wettability, or by pressure processes to force the latex into the fabric. The textile industry also makes use of the latex in flocking or piling operations. In the manufacture of rugs, upholstery, tapestries, and shoe or dress fabrics, short fibers are piled and held onto a fabric backing. The fibers, to prevent the necessity of mechanical interlocking, may be held in place by a film of latex compounded for adhesion and vulcanized for strength and chemical resistance. Fabrics combined with thicker films of latex are produced by a spreading operation. The wet film is spread to the desired thickness and allowed to dry prior to vulcanization. A film of rubber supported by fabric is thus obtained and may be used for tarpaulins, bed sheeting, shower curtains, and wet-weather garments.

Review Questions

1. Discuss the evidence which is of value in determining the structure of the rubber molecule.
2. Describe the preparation of smoked sheet rubber from latex.
3. Show by structural formulas the difference between rubber and gutta-percha.
4. What is the theoretical explanation of elasticity?
5. What is the cause of "plastic flow"?
6. Explain the meaning of "hysteresis"?
7. What is the purpose of adding each of the following substances to rubber:

³ Hauser, *Uses of Latex in the Textile Industry*, Rayon Textile Monthly, Sept. 1937.

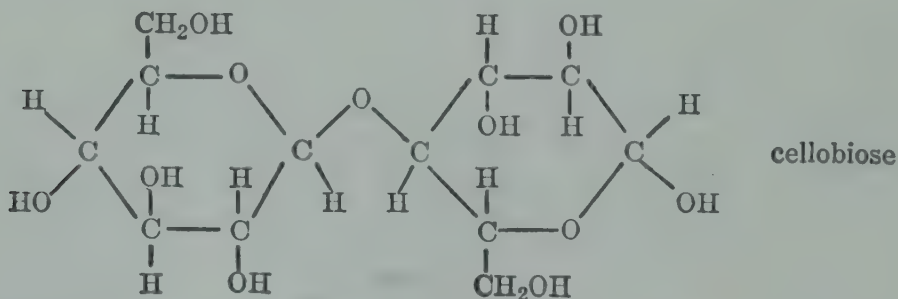
- (a) reinforcing agents
 - (b) accelerators
 - (c) low-melting coal tar resins
 - (d) mercaptobenzothiazole
 - (e) phenyl- β -naphthylamine?
8. Summarize the steps involved in the compounding of a typical rubber stock.
9. Describe the process used in making
- (a) rubber tubing
 - (b) molded rubber articles
 - (c) frictioned fabrics
 - (d) skim-coated fabrics.
10. Describe the following methods of making rubber products from latex:
- (a) electrodeposition
 - (b) dipping
 - (c) molding.
11. What methods are available for concentrating rubber latex?

CHAPTER IX

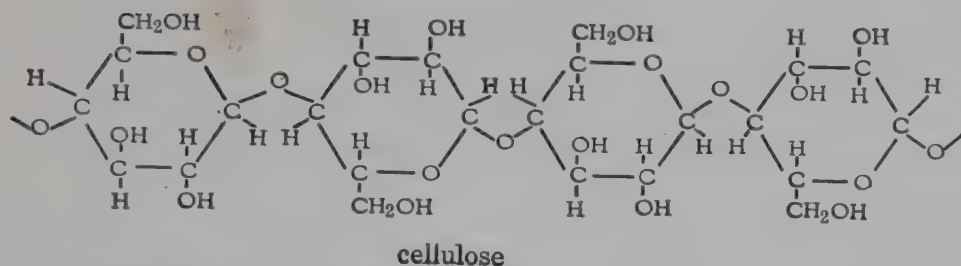
NATURAL PRODUCTS II: CELLULOSE

Cellulose is one of the most widely distributed and most useful products of the class of macromolecules. It is only natural, therefore, that a great deal of experimentation has been conducted in an effort to determine its composition and structure and to explain its chemical and physical behavior. Cellulose is the name given to linear polymers of glucose and it can be considered as a polyanhydride of glucose. The most important sources of cellulose are wood, cotton, flax, and hemp. Not all samples of cellulose are identical because differences in the lengths of the polymer chains and in the extent of association of individual polymer molecules to form micelles cause variations in the properties of different specimens of cellulose.

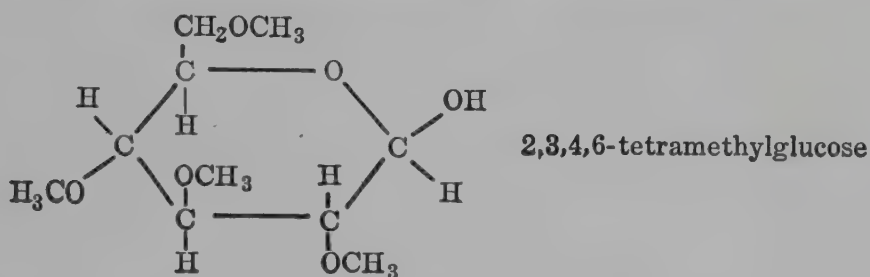
Structure.—The empirical formula for cellulose is $C_6H_{10}O_5$. Since complete hydrolysis of cellulose results in the exclusive formation of glucose, it follows that cellulose is a polyanhydride of glucose. Although it is believed that cellulose is formed from glucose in the plant, this synthesis has never been accomplished in vitro. Further evidence concerning the structure of cellulose was obtained when cellobiose was isolated among the partially hydrolyzed products of cellulose. Cellobiose is a disaccharide which has a β -glucosidic linkage between the two monosaccharide residues.



It is now believed that the cellulose molecule consists of a long chain of cellobiose units joined together by means of β -glucosidic linkages.



The most logical assumption to make concerning the terminal groups of the cellulose molecule is that they are hydroxyl groups. Evidence to support the idea that there are four hydroxyl groups in the terminal glucose residue at the left of the above formula is found in the isolation of a small amount of 2,3,4,6-tetramethylglucose among the hydrolysis products of a completely methylated cellulose.



While there is not such good evidence for the terminal hydroxyl group at the right of the above formula, this formula represents the accepted structure of the cellulose molecule. The number of cellobiose units involved is, of course, dependent upon the molecular weight of the cellulose sample. It is indicated further that the chemical structure of native cellulose, depending on its origin and history, may include miscellaneous groups along the chain. These may be carboxyl groups in place of $\text{—CH}_2\text{OH}$ (due to oxidation processes of nature), internal cross-linkages as by esterification to form a partial net structure, and side reactions with oxycellulose, hemi-cellulose, and lignin.

Molecular Weight Determination.—Determination of the actual chain length by the usual methods of osmosis or viscosity in solution is difficult in the case of cellulose because of the absence of a solvent which may be used without danger of rupturing the linear molecule. Figures obtained by employing such methods, with cellulose or with soluble derivatives, represent minimum values for the molecular weights involved. Determination of the molecular weight by x-ray methods also produces values which denote the lowest possible chain

lengths which may be involved for, in effect, this is a measurement of the length of the crystalline regions.

The wide variation in the molecular weights of different samples and the unreliability of the methods used is best exemplified by the broad range of values recorded by workers in this field. By means of x-ray determinations, the minimum values are in the vicinity of 30,000; by such general methods as osmosis, viscosity, or ultracentrifuge, values as high as 400,000–450,000 are obtained. Thus, no definite (or even approximate) molecular weight can be assigned to the cellulose molecule. However, the use of any one method in a series of molecular weight determinations will give comparable results. In this way it has been shown that the original source of the cellulose and its treatment prior to the molecular weight determination are important factors in determining the length of the cellulose chain. Also, comparative results of any series of measurements have shown that the polymeric molecular weight is an average value of the heterogeneous chain lengths present. The factors of both average size and weight distribution vary according to the history of the cellulose sample. A relative measure of the homogeneity of the sample may be made by fractional precipitation or fractional solution. The possibility of occasional cross-linkages between chains and the possible existence of micelles further complicate the determination of molecular weights.

Physical Structure.—The physical relationships which are existent between the cellulose macro-chains may be outlined by a considera-



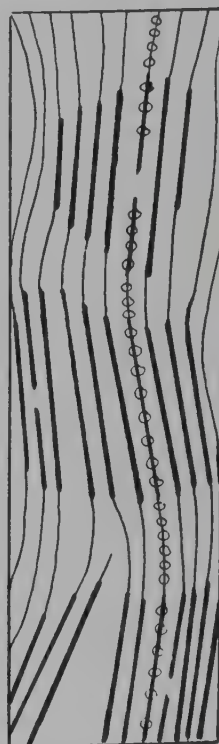
FIG. 9.1. X-ray diagram of native cellulose. (Marsh and Wood, *Introduction to Cellulose Chemistry*, p. 398, D. Van Nostrand Co., New York.)

tion of the crystalline structure of cellulose as depicted by x-ray analysis. When the inter-chain dependency has been established by picturing neighboring polymeric chains as parts of crystalline cells, the arrangement of glucose units within each chain will be better understood.

When cellulose is subjected to x-ray study the typical diagram obtained shows that a high degree of crystallinity exists in the cellulose fiber. A representative fiber diagram is pictured in Figure 9.1. The sharp outlines of intensity indicate the arrangement of cellulose chains, or at least some parts of them, in an oriented parallel, crystalline system. More elaborate study and measurement of distances involved have resulted in specific measurements of the crystalline regions. The actual crystalline positions, for it is generally agreed that amorphous divisions are interspersed along the molecular chain, are pictured as existing parallel to the fiber-axis and covering, on the average, a distance of 600 Å in length and 60–70 Å in width. These submicroscopic areas of oriented molecules are termed crystalline micelles. As previously defined, micelles, when used in reference to solid bodies, are “bundles of associated molecules” (Figure 9.2) bound by intermolecular attractive forces and arranged in crystalline order.

Also, the crystalline regions of cellulose differ from those of rubber in that their ability to behave and remain as a crystalline lattice is more permanent. Geometrical measurements and chemical behavior typical of the micellar lattice result from the higher lattice energy associated with the crystalline state.

The importance and the very existence of the amorphous regions in the cellulose fiber which separate the micelles from one another are illustrated by the variations in molecular weight determinations. When extreme care is exercised, values in the region of 200,000 to 400,000 have been obtained by Staudinger's method. The same samples, however, have shown molecular weight values of only 30,000 when the chain length is determined by x-ray



Cellulose Micelles

FIG. 9.2. The association of molecules to form micelles is shown by the dark areas. (Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 252, Interscience Publishers, Inc., New York, 1942.)

data. The chain length measured is only the length of the chain (600 Å) involved in a crystalline area.

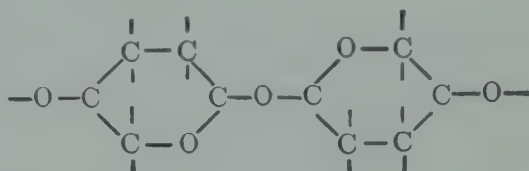
Measurement of the x-ray diagrams has clarified the submicroscopic structure further. Just as in the case of sodium chloride a unit cell (repeating unit) may be defined, so too, is it possible to outline the arrangement and dimensions characteristic of the cellulose unit cell. The following dimensions along crystal axes have been determined:¹

$$a = 8.35 \text{ Å}$$

$$b = 10.3 \text{ Å (fiber-period of repetition along fiber axis)}$$

$$c = 7.9 \text{ Å}$$

From these data and a knowledge of the specific gravity of cellulose the unit cell may be characterized as consisting of four glucose residues. The crystalline chain which is formed, therefore, as one unit cell follows another, lies parallel to the fiber-axis along a nearly straight line. Consideration of interatomic distances and valence angles leads to the conclusions: (1) that only a slight inclination of the chain with respect to the fiber axis occurs; (2) that along the crystalline chain each ring is rotated through 180° with respect to its neighboring ring. When the proper values of interatomic distance and angles are assumed, the identity period of approximately 10.3 Å as measured by x-ray may be pictured:



This indicates that cellulose is composed of cellobiose units.

Reactions of Cellulose.—The broadest classification of the reactions involving cellulose is that which is based upon the relationship of the reactions to the micellar structure. Meyer² lists the two types: intermicellar reactions (micellar surface reactions) and intramicellar reactions.

1. Intermicellar Reactions. As the name implies these are reactions which do not disturb the interior of the micellar arrangement in the cellulose product. The surface of each bundle is the only portion actually affected by any changes which might occur. Such

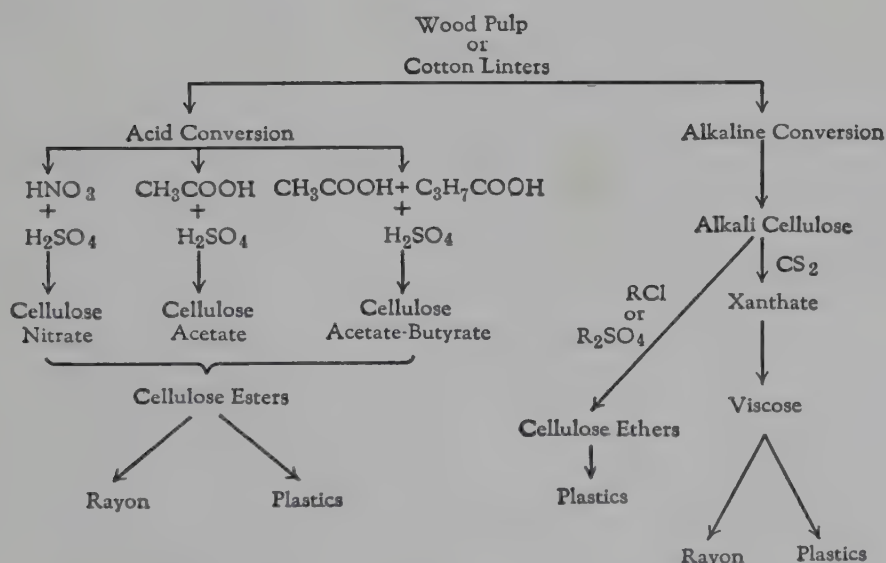
¹ Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 239, Interscience Publishers, Inc., New York, 1942.

² Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 265, Interscience Publishers, Inc., New York, 1942.

changes as adsorption of mordants or miscellaneous metallic salts, reaction with effective dyes, and water sorption are typical of the intermicellar type. In general, the hydroxyl groups and occasional carboxyl groups (formed by oxidation of a few CH_2OH groups along the chain) are responsible for these surface changes.

2. *Intramicellar* reactions are directly opposite in type to the above group in that they destroy the micellar arrangement and involve the interior of the micelle. These reactions are of more general importance and interest than intermicellar reactions, particularly in the plastics field. Such chemical reactions as nitration, acylation and the formation of alkali cellulose are intramicellar reactions which cause the destruction of the crystalline micelles of cellulose. These reactions are accomplished with reagents which react with the hydroxyl groups of the cellulose molecule. The two most important reactions are esterification and etherification. Each

TABLE I-9



will be discussed in some detail when the plastic products formed by these reactions are considered. (See Chapter XII.) The relationship of the leading derivatives and the reagents used in their preparation are summarized in Table I-9. In all intramicellar reactions, a certain amount of degradation of the cellulose molecules occurs. The process of degradation is a breaking down or cleavage of the cellulose chain, usually by hydrolysis, acetolysis, or oxidation. The cellulose molecules on the outside of a micelle may undergo extensive degradation while those well inside the micelle may be degraded only

slightly or perhaps not at all. The degree or extent of degradation can be determined by comparison of the average molecular weight of the original cellulose with that of the reaction product. The principal effects of degradation are:

- (a) Increased chemical reactivity
- (b) Greater solubility in a wider variety of solvents
- (c) Solutions of lower viscosity
- (d) Loss of tensile strength.

Physical Properties of Cellulose.—Although the properties and behavior of the derivatives of cellulose are of greater interest than those of cellulose itself in a study of plastics, a brief survey of the principal characteristics of cellulose is valuable for purposes of comparison and prediction. In most instances no direct simple statement of the quantitative physical properties of cellulose may be made because of the variations in structure, degradation, and micellar arrangements. Qualitative relationships of various types may, however, be outlined. Characteristics which are of mechanical importance are of particular interest.

Tensile Strength.—The tensile strength of various cellulosic bodies is variable and is dependent upon a number of factors. Differentiation should first be made between natural or native cellulose fibers, e.g., cotton and ramie; and degraded fibers, e.g., artificial silk. In the first class are found threads composed of polymeric



FIG. 9.3. Native cellulose fiber showing long primary chains. (Meyer *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 330, Interscience Publishers, Inc., New York, 1942.)

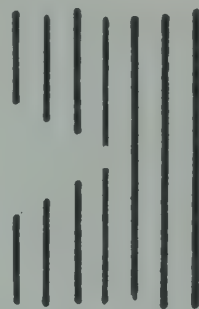


FIG. 9.4. Rupture of chains. (Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 330, Interscience Publishers, Inc., New York, 1942.)

chains held together by primary valence linkages running the entire length of the fiber. When stress is applied to such a structure, rupture may occur only as a result of cleavage of the primary valence

at some point in the chain, as shown in Figures 9.3 and 9.4. As a consequence, the tensile strength in such cases may be expected to exhibit unusually high values. The tensile strength of cellulose is approximately 40,000 lbs. per sq. in. This value compares very favorably with those of certain metals, as shown in Table II-9.

TABLE II-9. TENSILE STRENGTHS

Substance	Tensile Strengths in lbs. per sq. in.
Cellulose (native)	40,000
Cellulose acetate	2,000- 10,000
Cellulose nitrate	6,000- 9,000
Ethyl cellulose	6,000- 12,000
Aluminum wire	30,000- 40,000
Silver wire	42,000
Platinum wire	50,000
Steel	80,000-330,000

When dealing with artificial or degraded fibrous products, the fact that shorter chains and amorphous regions exist is proved by the lower tensile strengths exhibited (See Table II-9) and, particularly, by the dependence of the tensile strengths upon the secondary valence forces. In the rupture of this shorter-chained, less oriented structure, the slippage of the chains past one another is of primary importance. The degree of orientation, the chain length, the chemical nature of the chain, and the presence or absence of any plasticizing agent (including moisture) are all effective in the determination of the secondary valence force which will be exhibited. These intermolecular attractive forces, in turn, determine the ease with which the constituent chains will slip past one another. Under such conditions, it is not surprising to find that the tensile strength of these degraded fibers is somewhat lower than that of native cellulose. Figure 9.5 illustrates the fracture of a cellulose chain resulting from slipping.

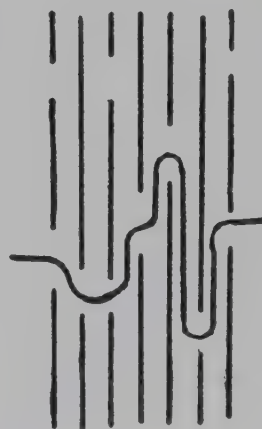


FIG. 9.5. Fracture of cellulose chains resulting from slipping. (Meyer, *Natural and Synthetic High Polymers*, High Polymers, Vol. IV, p. 330, Interscience Publishers, Inc., New York, 1942.)

Elastic and Plastic Properties.—With respect to elastic characteristics of cellulose fibers, the native cellulose fiber, with its highly oriented system, exhibits very different properties from the shorter-chained, less oriented, degraded fibers. The very high modulus of elasticity encountered in the case of native cellulose is explained by the fact that deformation or extension may be created only by displacing parts of the cellulose crystalline system. Distortion of atomic positions or valence angles is resisted by great forces and the high modulus is thus accounted for.

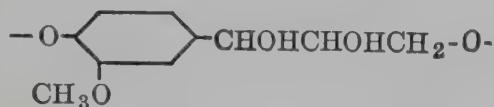
When the elasticity of rubber was discussed, (p. 130), the extension of spiraled chains or the slippage of molecular units over one another and their return, upon release of stress, to more probable positions, was used as the basis of the theoretical explanation. Similarly, in the case of cellulose and its derivatives, as the degree of crystallinity (oriented regions) decreases and as the movement of polymeric chains past one another becomes easier, as by incorporation of a liquid plasticizer, the amount of elasticity of the type described in connection with rubber increases. The cellulose ethers or esters, for example, contain a high proportion of amorphous structure and, as a consequence, elasticity is exhibited and is increased when the friction between molecules is reduced by plasticization.

The plastic properties of native cellulose are negligible when compared with the plastic tendencies of less oriented materials. The high degree of attraction between molecules which is caused by the hydroxyl groups present along the chain prevents plastic deformation in the absence of high stresses. When the effect of the hydroxyl groups is decreased by incorporation of swelling agents, deformation by plastic changes is more easily accomplished. Likewise, if by chemical reaction such as esterification or etherification the hydroxyl group is replaced by some less polar group, the internal friction is lowered to a point where plastic flow is possible. Even in such cases as these, however, the extent of plastic deformation decreases as the final chain length approaches the original chain length.

Composition of Wood.—Since wood is one of the most important sources of cellulose, a brief description of the most important methods of obtaining cellulose from wood will be given, together with a brief discussion of the plasticization of cellulose in the manufacture of paper.

For practical purposes, wood may be considered as consisting of approximately 60% cellulose bound in a cementing matrix of lignin. The structure of lignin is not definitely known. According to the

experimental evidence obtained to date, lignin appears to contain double bonds, aromatic nuclei, and methoxyl groups. A typical group which is believed to be present as part of a more complex structure is:



Although lignin was previously considered as a useless by-product of the manufacture of cellulose from wood, it is gradually rising to some degree of importance as a plastics molding material.

The true industrial significance of wood, from a chemical point of view, lies in the desirable properties of the cellulose which can be separated from the cementing matrix of lignin. In this separation process the intermediate product *chemical wood pulp* is formed. The method by which it may be produced depends upon the type of wood being treated, the product desired, and the conditions under which the manufacture is completed. The three most important processes for the separation of cellulose from lignin are the sulfite process, the soda process, and the sulfate process.

Sulfite Process.—The principal method, at the present time, is known as the sulfite process because of the use of sulfurous acid and the resultant formation of sulfites in the process. The process is not limited to any particular type of wood, but the most satisfactory results are obtained by its use in the processing of coniferous woods such as spruce or fir, both of which contain a low percentage of resin. The chemical changes involved in the production of chemical wood pulp consist essentially of solution of the lignin by reaction with the sulfurous acid. To reduce the possibilities of side reactions with their accompanying formation of undesirable products, the acid solution is buffered with calcium or magnesium bisulfites. The reaction is usually carried out at a temperature of approximately 140° C., under a sulfur dioxide pressure of 80 lbs. per sq. in., for a period of 8–12 hours. After washing or “blowing” from the accompanying sulfite liquor, the pulp is ready for further processing.

Soda Process.—This method is similar to that previously described but is particularly useful for deciduous trees such as poplar. Solution of the lignin, in this case, is accomplished by the use of a 7–8% caustic soda solution kept at approximately 170° C., for 4–6 hours. The “black liquor” which results contains dissolved lignin in the form of salts of organic acids. After separation of the pulp, the black liquor is evaporated to dryness and the residue ignited in

order to recover sodium carbonate. A small percentage of the cellulose is also carried off in the "black liquor" and lost. The recovered pulp, however, evidently contains the cellulose in approximately the same degree of polymerization as that in which it occurs in the wood.

Sulfate Process.—This method is preferred with woods of high resin content such as Southern Pine and in processes in which a fibrous pulp is desired. The solution used for treatment contains principally caustic soda, but in this case, its action is modified by the presence of sodium sulfide (obtained from sodium sulfate) and sodium carbonate. The sulfide appears to be the active agent in dissolving the lignin, for mercaptans and organic disulfides are found in the residual liquor. In addition, however, the sulfide reduces the strong chemical action of the caustic soda, and thus permits the formation of the pulp without harmful effects on the cellulosic fiber. The sodium carbonate is comparatively inert.

The prepared pulp is freed from contaminating liquor by washing. The liquor in turn is processed to recover much of the sodium sulfide after combustion, and the sulfide lost is replaced by sodium sulfate. The sodium sulfate is added before the liquor is evaporated to dryness. When dry, the residue is ignited (heated strongly) in order to destroy the organic matter. During this combustion the added sodium sulfate oxidizes some of the organic matter and is reduced to sodium sulfide.

Paper Manufacture.—The first step involved in the formation of most industrially useful products from chemical wood pulp is *bleaching*. The processing methods of particular interest are one-stage and two-stage operations. The former is carried out merely by treatment of the screened, washed pulp with such an agent as calcium hypochlorite in a solution having a pH of 8–11.

In the two-stage process, however, the aqueous suspension of the pulp is first treated with chlorine. The hydrochloric acid thus formed provides a strong acidity, while the chlorine removes colored impurities by the formation of chlorine derivatives which are dissolved in the second stage. This operation, which consists of washing the wood pulp with alkali, completes the bleaching process. Excess hypochlorite may be removed by the addition of sodium thiosulfate and all water soluble substances may be removed by washing the fiber with water.

With proper control of time, temperature and pH, and the complete removal of the reagents used, no appreciable degradation of the cellulose molecule or weakening of the fiber results. At this point,

then, the cellulose fibers have an amorphous structure, are resistant to physical and chemical action, and are incapable of coalescence or adhesion. The tendency to coalesce, sometimes called the plasticity factor, may be increased by treatment with polar liquids. When subjected to the action of such materials as water, ethylene glycol, formamide, or ethyl alcohol, swelling with its accompanying increase in plasticity or coalescence results.

The most important operation in the formation of certain paper stocks is possible only because of this typically plastic-like effect of swelling. This operation is known as *fibrillation* and, in effect, it consists of beating the cellulose fibers while they are maintained in the swollen condition in a polar liquid medium. Mechanical mastication causes rupture of the weakened fiber walls and countless fibrils are formed by the agitation. The definite dependence of fibrillation upon the polarity of the medium and its absence in non-polar liquids has been established.

The paper which then results from deposition of the fibers in a mat, i.e., *matting*, varies with the degree and efficiency of the fibrillating process. The greater the extent of fibrillation the more closely the fibers are packed together and the greater the strength of the paper produced.

From a chemical point of view, the cellulose fibers are bundles containing a very large number of cellulose molecules. In such large bundles, only a few of the molecules, those on the surface, are exposed to the action of the water. In order to break up these bundles so as to expose more hydroxyl groups to the action of water, thereby facilitating and accelerating the effects caused by water, the fibers are beaten mechanically. The physical effect produced by beating is known as fibrillation and the chemical effect is known as hydration. The subdivision of the cellulose fibers to fibrils may be so extensive that the paper formed is translucent or even transparent. The hydration of the fibrils facilitates their coalescence into a compact mass of paper.

The effect of various solvents on the paper illustrates its behavior under plasticizing conditions. Water causes the material to swell and lose a portion of its strength; benzene, on the other hand, has little or no effect upon the cellulose. The plasticizing effects, therefore, result in individual swelling of the fibers and loss of coalescence while wet. Peculiarly, the same chemical substance—cellulose—when it exists as in a cotton fiber, may be strengthened by the plasticizing action of water. In this case, the increased plasticity permits

the fibers to slip over one another and, thus distribute the loading force over all parts of the structure.

When these methods of plasticization have been applied to a degree consistent with the grade of paper desired, the final operations of *sizing* and *cutting* may be carried out. The former process is that of introducing a bonding material around the cellulose fibers to cement them into a composite whole. A rosin soap mixed with alum is typical for this use, for in such a product, the aluminum salt of rosin is obtained. This exhibits excellent water repellancy and bonding strength.

Review Questions

1. Give the name and formula of the repeating unit present in the cellulose molecule.

2. What conclusions have been made relative to the molecular weight and crystallinity of the cellulose structure? What is the evidence?

3. What functional (reactive) groups are present in the cellulose molecule? What types of reactions is cellulose subjected to in the preparation of commercial plastics? Write equations for these reactions.

4. Summarize the composition of wood.

5. Why is:

(a) fibrillation

(b) plasticization by water

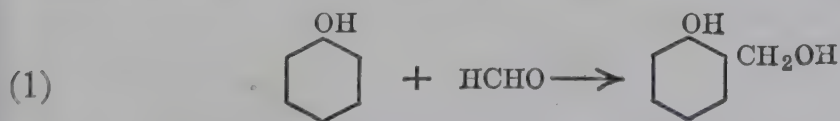
important in paper manufacture?

CHAPTER X

SYNTHETIC PLASTICS I: THERMOSETTING PHENOLICS

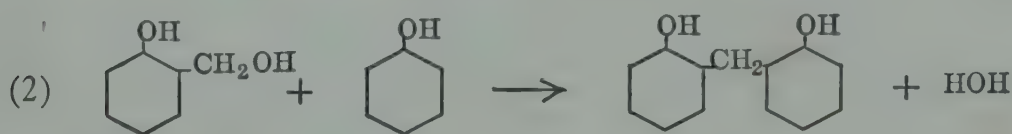
When the term "phenolics" is applied in the plastics industry the molding compounds sold as *Bakelite* products come to mind. The meaning of the term is much broader, however, for it may include all materials prepared from phenol or other aromatic phenolic compounds combined with formaldehyde or other aldehydes. The applications embrace a multitude of possibilities in all branches of the plastics trade—molding, casting, laminating, coatings. The association of the terms "phenolic resin" and "Bakelite" dates from the first practical introduction of phenolic resins in 1907 by Baekeland. Although the history of the reaction between phenols and aldehydes may be traced back to the early part of the nineteenth century, the original investigators of the reaction were not concerned as much with the resinous product obtained ultimately by heating, as they were with the intermediate crystalline products first formed in the reaction. When Baekeland showed that the final resinous product was of specific interest in industry for the formation of molded products, work on these derivatives and others of similar nature was stimulated. The fundamental investigations carried on by the research department of the Bakelite Corporation and by many other workers in this field have contributed a great deal to our knowledge of the mechanism of the reactions involved. As a result of this research, it is possible to vary the composition and hence the properties of the phenolic resins over quite wide ranges. So many different products have been made for such varied uses that they are sometimes referred to as "tailor-made."

Chemical Reactions.—The reaction between formaldehyde and phenol may be represented by the following equation:

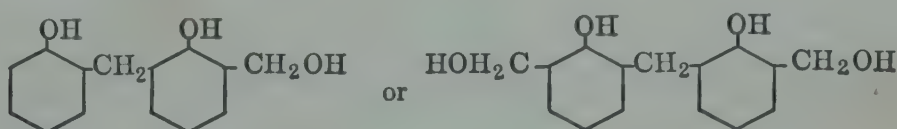


It is well-known that the hydrogen atoms in the ortho and para positions with respect to the phenolic hydroxyl group are quite reactive. The reaction may be considered as the addition of one of

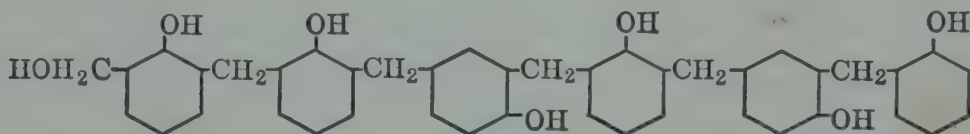
these active hydrogen atoms to the carbonyl oxygen of formaldehyde followed by the attachment of the benzene ring to the carbon atom of the formaldehyde molecule. The alcoholic hydroxyl group of *o*-hydroxybenzyl alcohol is quite reactive and hence this alcohol can condense with another molecule of phenol as follows:



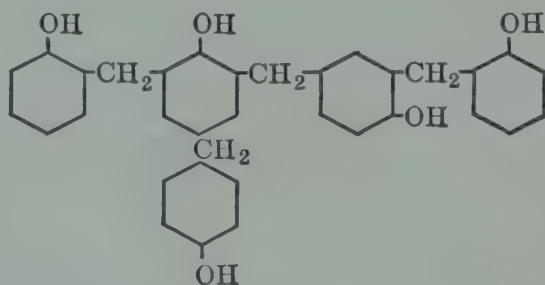
This 2,2'-dihydroxydiphenylmethane can add to one or two molecules of formaldehyde forming



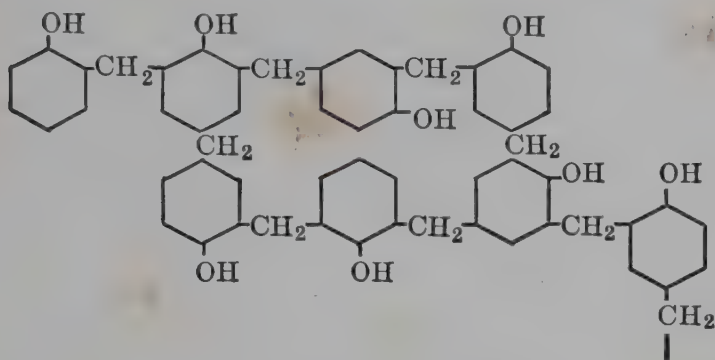
These compounds can react with one or two molecules of phenol as in equation (2). The continued repetition of these reactions of addition and condensation will lead to the formation of a linear polymer, e.g.,



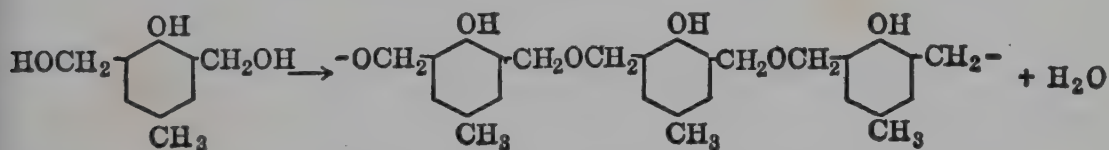
Whether the end groups are methylol groups or phenolic rings will depend upon the relative amounts of phenol and formaldehyde used in the reaction. In this formula, each aromatic ring has one hydrogen atom which is either para or ortho to a phenolic hydroxyl group. These hydrogen atoms may also enter into a reaction with formaldehyde forming first a branched-chain polymer, e.g.,



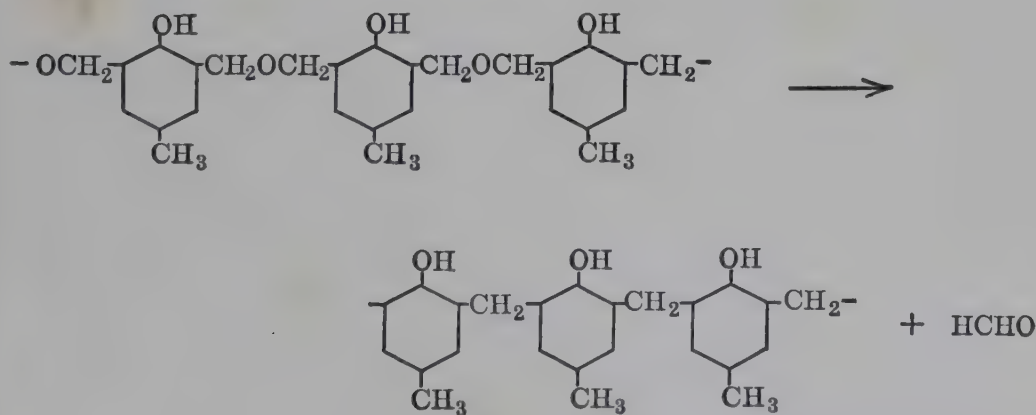
and eventually a cross-linked polymer, e.g.,



It has been postulated that the conversion of the phenol-alcohols to a polymeric form proceeds through the formation of ether linkages:

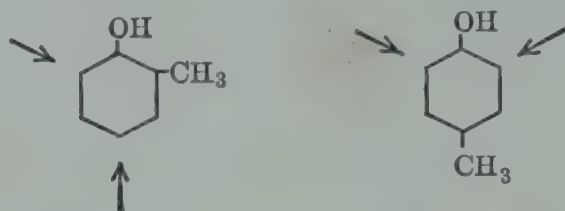


Gentle heating of the dimethylol phenol causes the elimination of water without any appreciable loss of formaldehyde. When heated to a higher temperature, the mixture gradually loses one molecule of formaldehyde for each phenolic group present in the chain, thereby forming the typical methylene linkage between the aromatic rings, e.g.,



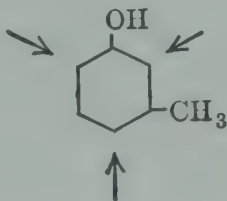
In the light of the preceding discussion concerning the nature of the phenol-formaldehyde reaction, it is interesting to consider the types of reaction which are possible with certain homologs of phenol. Examination of the formulas for ortho and para cresol reveals the fact that there are only two active hydrogen atoms in each of these

molecules. These are indicated by the arrows.



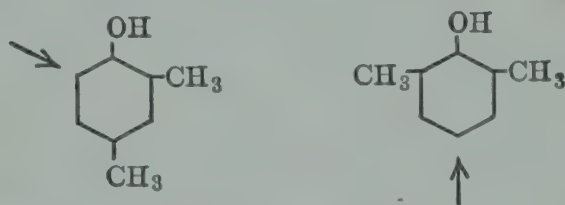
These compounds are capable of forming linear polymers only.

The formula for *m*-cresol, on the other hand, shows the presence of three active hydrogen atoms.

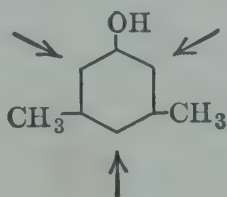


This compound is therefore capable of forming a cross-linked polymer with formaldehyde.

2,4-Xylenol and 2,6-xylenol have only one active hydrogen atom, as indicated in the formulas:



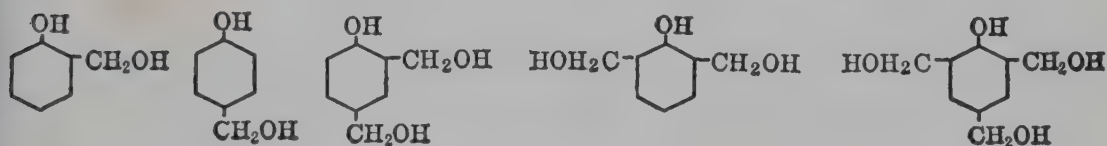
These compounds are incapable of forming linear polymers with formaldehyde. 3,5-Xylenol has three reactive positions, and hence is capable of forming a cross-linked polymer.



Since commercial phenol obtained from coal tar is likely to contain varying amounts of these homologs of phenol, it is necessary to control the nature and amount of these impurities in order to

produce a uniform product. Ortho and para cresols cause a decrease in the number of cross-linkages with consequent decrease in the hardness and heat resistance of the finished product. Xylenols (2,4- and 2,6-) slow down or may even stop the reaction. However, it should be pointed out that the cresols and related phenols (particularly *p*-tertiary butyl phenol) are of considerable value in making linear polymers which are soluble in drying oils and hence useful in lacquer formulations.

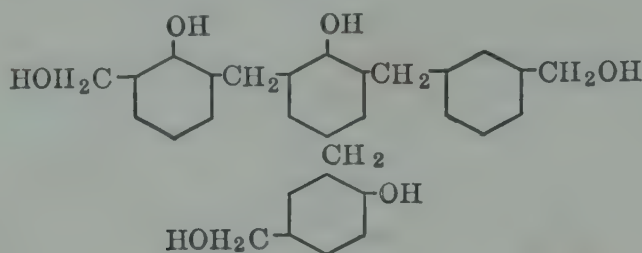
The catalyst employed, together with the proportions of phenol and formaldehyde used, are very important factors in determining the mechanism by which the reaction occurs. When an alkaline catalyst is employed, an excess (usually 1.5:1, measured in equivalents) of formaldehyde is used. The first step in the reaction involves the addition of a molecule of phenol to one, two, or three molecules of formaldehyde. Of the five theoretical possibilities,



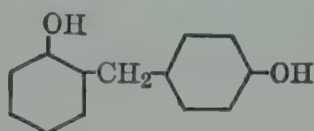
only the first two have been isolated from the interaction of phenol and formaldehyde in an alkaline medium and identified definitely. Granger¹ has apparently isolated the other three compounds as syrupy liquids, but they have not yet been positively identified. *p*-Cresol, however, forms a well-defined, crystalline dimethylol derivative which forms a resin when heated. The first of the above compounds, namely *o*-hydroxybenzyl alcohol (saligenin), has been known for many years and can be transformed into a resinous substance simply by heating. All of these molecules containing methylol groups can condense with phenol molecules. The excess of formaldehyde present in the reaction mixture leads to the introduction of more reactive methylol groups. Chain-branching and eventually cross-linking occur. The reaction is carried out by heating the mixture. If the reaction is stopped during the early stages, simply by lowering the temperature of the reaction mixture, a soluble product known as a resol is obtained. As the reaction proceeds, however, the solubility of the resol decreases, as a result of the formation of cross-linkages. A resol reaches a molecular weight of 300-400 before showing signs of becoming insoluble. A typical resol

¹ Granger, *Ind. Eng. Chem.* **24**, 443 (1932).

form is shown by the graphic formula:



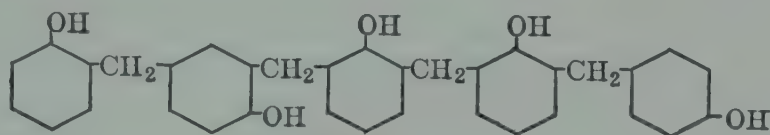
When an acid catalyst is used, somewhat less than the theoretical amount of formaldehyde is heated with phenol. In this case the first products which have been isolated from the mixture are 2,2', 2,4'- and 4,4'-dihydroxydiphenylmethane.



2, 4'— dihydroxydiphenylmethane

Since an insufficient amount of formaldehyde is employed in conjunction with acid catalysts, the formation of $-\text{CH}_2\text{OH}$ groups or cross-linkages is limited. Although the phenol alcohols may be the initial products formed they are so rapidly converted by the excess of phenol to diphenylmethane derivatives that they cannot be isolated.

As the formation of the substituted methane type of product continues, the resin form known as *Novolak* is gradually produced. The Novolak resin consists of a chain which usually contains five or six phenolic residues, but which is capable of having a molecular weight as high as 1500. Since cross-linking does not occur to any appreciable extent in a Novolak resin, solubility in suitable organic solvents is maintained to a much higher molecular weight than in the case of resols.

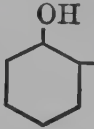


Novolak Resin

In order to change the fusible, soluble Novolak resin into a cross-linked thermosetting resin, it is heated with some hexamethylene-tetramine, $(\text{CH}_2)_6\text{N}_4$. Under the experimental conditions, hexa-

methylenetetramine decomposes to form both formaldehyde and ammonia. With ammonia acting as a catalyst, the formaldehyde reacts with the phenolic rings forming methylol groups. The methylol groups on one Novolak chain may react with the phenolic rings of one or more chains forming cross-linkages. As these cross-linkages develop in the final hardening of a Novolak resin, the molecular weight increases rapidly. A partial formula for the hardened resin is illustrated on p. 165.

The relationship of the two products, resols and Novolaks, may be clarified by a brief comparison of the methods of preparation:

1. Phenolic alcohols  CH_2OH are probably formed as the first product in both cases.

2. The two processes differ in their speed of conversion to the second product—a diarylmethane derivative. With acid catalysts the reaction between a methylol derivative and a phenol occurs rapidly; with alkaline catalysts, this reaction is slow, so that the principal reaction is simply the introduction of methylol groups.

3. In the final hardening of a Novolak resin, the ammonia from the hexamethylenetetramine catalyzes the introduction of methylol groups. The resols can harden because of the excess methylol groups already present. The elevated temperature is believed to be the main factor in causing cross-linkages in both cases.

Considerable experimental work has been done concerning the catalysts used for the formation of both resols and Novolaks. Although sodium carbonate and ammonia are the most commonly used alkaline catalysts, others such as sodium, potassium, and calcium hydroxides, magnesium phenoxide, quaternary ammonium hydroxides, and urea have been found satisfactory. Acid catalysts which have been successful in catalyzing this type of polymerization are hydrochloric, sulfuric, formic, tartaric, and aromatic sulfonic acids. Resins prepared by the use of an acid catalyst are formed 3–3.5 times faster than those made with an alkaline catalyst, provided the same amount of formaldehyde is used in each case. When an acid catalyst is used, the velocity of resinification is proportional to the concentration of acid used, whereas the velocity, using an alkaline catalyst, is largely independent of the concentration of the catalyst. When polyhydroxyphenols are used in place of phenol, no catalyst is required.

Suitable agents which facilitate the final hardening (third stage) of phenol-formaldehyde resins are acids, alkalies, hexamethylenetetramine, esters of sulfuric acid, acid chlorides, resorcinol, ferric chloride, and titanium tartrate.

Manufacture.—The manufacture of phenolic resins is usually carried out by a wet process involving the use of 37% formalin solution. The actual details of manufacture are not complicated for they involve only regulation of the ratio of reactants and the physical conditions of temperature and pressure.

Although numerous variations are possible, both with respect to ingredients and experimental conditions, the following formula may be considered as representative:

Phenol	40 lbs.
Formaldehyde (37%)	52 lbs.
Sodium Carbonate	0.8 lb.

These ingredients are placed in a jacketed autoclave which is then heated to a temperature of 95° C. for 1–1½ hours. At this temperature the resinous mass may be dehydrated simply by venting the



FIG. 10.1. Phenol-formaldehyde resin being poured onto a canted floor.
(Courtesy of Monsanto Chemical Co.)

autoclave. If a lower temperature is used, it is desirable to remove the water by distillation under reduced pressure. When dry, the molten resin is dropped from the autoclave into cooling pans or onto a cooling floor (Figure 10.1), from which it may be removed, ground, and compounded. In the case of casting operations, the control of the reaction is regulated to the production of a liquid or semi-solid resinous mass which may be compounded with plasticizers and pigments in the reaction kettle after partial dehydration.

The manufacture may be carried out as a one-step or a two-step process. In the one-step process, an alkaline catalyst (sodium carbonate or lime) and an excess of formaldehyde are used. Mole ratios of phenol to formaldehyde of 1:1.5 up to 1:3 have been used with 1–5% catalyst. The reaction may be interrupted after the formation of molecules containing two or three aromatic rings, (start of resol formation) for application of the resin to casting or laminating procedures.

The two-step phenolics are formed by the use of an acid catalyst (HCl or H_2SO_4) and an insufficient amount of formaldehyde. The ratio of phenol:formaldehyde is generally about 1:0.8, and 0.5–1% of

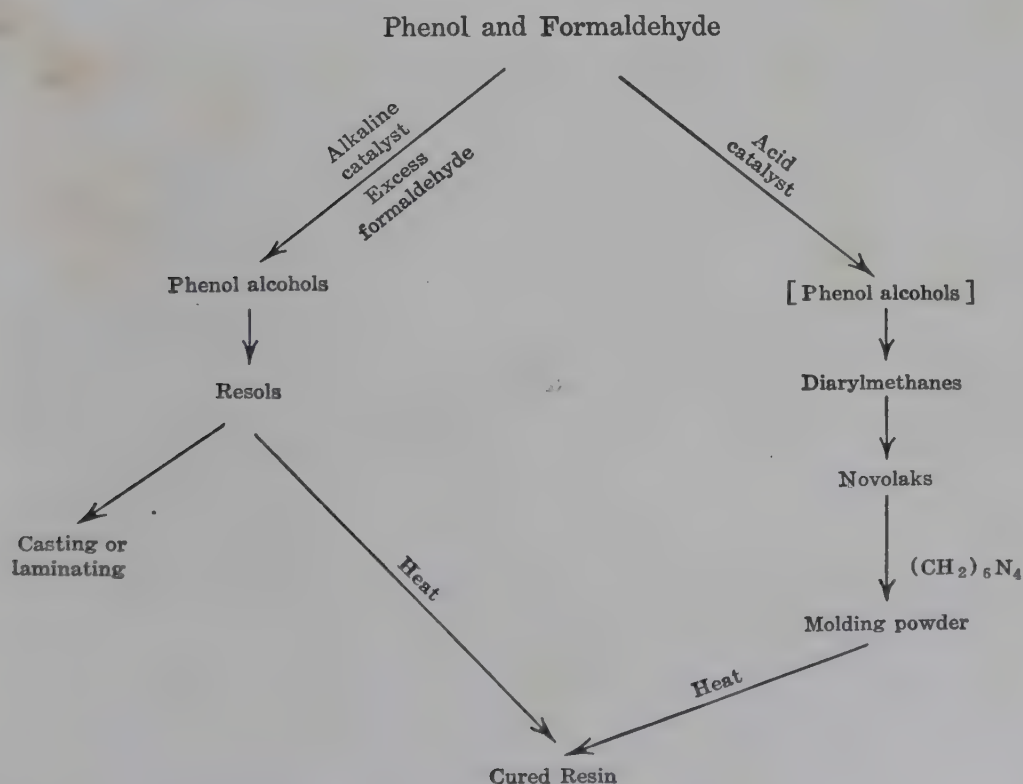


FIG. 10.2. The stages of formation of the phenolic resin by either method are referred to as A, B, and C stages of manufacture.

an organic or inorganic acid is used as the catalyst. The reaction proceeds to the formation of a solid Novolak which may be ground and compounded to form a molding powder, or may be used in the manufacture of a lacquer which is suitable for laminating purposes. In each case, the final curing takes place only after addition of the hardening agent—hexamethylenetetramine—which supplies the required amount of formaldehyde and also provides an alkaline catalyst. The chart (Figure 10.2) shows the relationship of these methods. Although the division of products into these three groups is rather indistinct because of overlapping, the following general descriptions apply:

A Stage: This stage involves the formation of an initial resinous product. The latter is thermoplastic and completely soluble in alcohol.

B Stage: By continued heating of the "A" stage resin at moderate temperatures, the intermediate form of a fusible but difficultly soluble resin is produced. This is known as a "B" stage type.

C Stage: The final product, characterized by its infusible and insoluble properties, is formed as the "B" stage resin is heated in the presence of sufficient formaldehyde to cause curing.

The three stages represent a gradual conversion from the raw materials of phenol and formaldehyde to the final, hardened product. The actual conversions are gradual so that no sharp dividing line separates any stage from those preceding or following it.

MOLDING POWDER PHENOLICS

In the production of molding powders, the first problem is to prepare the most suitable phenol-formaldehyde resin, which, when properly compounded and cured, will yield a product having all of the properties desired. Since phenol, cresols, xylenols, and even resorcinol can be used either singly or mixed in any desired proportion, it is evident that numerous resin bases, each possessing different characteristics, can be obtained. By controlling the degree of polymerization before compounding and curing, still further variations in properties are possible.

Resins which are to be used in molding powders are usually prepared by the two-step process as described on p. 171. Such compounding agents as dyes, pigments, plasticizers, lubricants, and fillers (asbestos, wood-flour, mica, fabric, or clay) are thoroughly incorporated with the ground resinous base. This mixing is usually done on heated rolls where full kneading action insures complete

homogenizing. The temperature is controlled so that the resin is in a soft, plastic state. If the temperature is too high or is held over too long a period, the plastic mass may thicken or even harden. The amount of mixing often serves as a means of regulating the softening point and the flow of the plastic in the mold. When the completely compounded mixture is cooled and ground to the desired particle size, the molding powder is available for use. The fillers used for each particular type of molding powder are chosen because of the value of certain properties imparted. Table I-10 summarizes the most common types:

TABLE I-10. TYPES OF PHENOLIC MOLDING POWDERS

Type of Molding Powder	Filler Used	Applications
General purpose	Wood flour	Door knobs, refrigerator parts, telephone sets
Cellulose-filled, impact resistant	Cellulose (cotton)	Closures, advertising displays
Heat resistant	Asbestos	Ash tray, heater plug
Impact resistant	Canvas (fabric)	Vibrator case, oil-well drilling equipment
High dielectric	Mineral (mica)	Electrical connector, insulation cases

Plasticizers are of secondary importance and are often omitted. Coloring agents are, for the most part, coal tar dyes or inert pigments (iron oxide, bone black). The dyes are preferred in applications requiring high dielectric strength. A combination of dyes with inorganic pigments produces a uniform dispersion and bright tone. Lubricants are metallic soaps, stearates, or stearic acid. The formulation of molding powder and the softening point of the base resin leads to a subdivision of molding powders into classes of soft, medium, and stiff flow.

When the final stage of curing or hardening of the molding powder is reached, it is found that the temperature, pressure, and molding cycle² are dependent upon the composition and previous treatment of the powder. Such variables as the phenolic compounds used in the preparation of the base resin, the degree of polymerization, the nature of the compounding agents, the period of mixing, and the

² Molding cycle is the time required for the molding process of the compound—closing of the mold, curing, and ejection from the mold.

amount of hexamethylenetetramine added to effect the final cure are important factors in determining the proper conditions for the cure. Consequently the temperature, pressure, and molding cycle of each powder must be determined before final application. Overcure of phenolic materials, however, does not have the harmful effect noticeable with other materials. Although the molding powder manufacturer often recommends particular conditions, the custom molder must often adapt the powder to his own particular needs.

Properties and Applications.—Many of the general characteristics of molded phenolics may be predicted from knowledge of the fact that a thermosetting resin is involved. A suitable molding powder for almost any application may be selected from the list of diversified, specialized types.

Although certain factors such as impact strength, heat resistance, and electrical strength vary, depending on the filler involved in compounding, certain other properties remain generally characteristic. The phenolics, for example, are noted particularly for the poor colorability of the molded products. Although high gloss may be produced, color stability is rarely realized. General resistance of the cured material to non-oxidizing acids, moisture, organic solvents, and resistance to temperatures as high as 205° C. for prolonged periods, are characteristics usually associated with molded phenolics. At best, the resistance to alkalies is only fair, and they are decomposed by oxidizing acids.

The electrical properties of molded phenolic resins vary over quite wide limits depending upon the type of filler used and the completeness of removal of the acid or alkali used as a catalyst for the poly-



FIG. 10.3. Telephone hand set and housing molded from phenol-formaldehyde polymer. (Courtesy of Bakelite Corporation.)

merization. For example, the dielectric constant varies from 4 to 20, and the power factor varies from a low of 0.007 for a mineral-filled resin to a high of 0.3 for a resin in which wood flour is the filler. Obviously, the best electrical properties are obtained when the acid or alkali used for polymerization has been removed most completely.

The mechanical properties also vary widely depending upon the formulation used. Tensile strengths vary from 4,000–11,000 lbs. per sq. in.; compression strengths vary from 16,000 to 36,000 lbs. per sq. in.; flexural strengths vary from 10,000–15,000 lbs. per sq. in.; and impact strengths vary from 0.11–2.4 ft.-lbs. The values obtained for these mechanical properties depend upon the homogeneity of the cured resin as well as the compounding; the more homogeneous product having the higher values.

The applications of molded phenolics are widespread. Such a diversified list as:

Radio parts	Machine housing
Junction boxes	Telephone equipment (Figure 10.3)
Distributor caps	Aircraft parts
Valves	Protective helmets
Electrical insulation	Tool parts
Clock cases	Camera cases
Slide fasteners, replacing metallic zippers	
Agitators in washing machines (Figure 10.4)	



FIG. 10.4. Washing machine agitator molded from phenol-formaldehyde polymer: (Courtesy of Bakelite Corporation.)

is representative of the type of product manufactured from this class of phenolic. New developments and improvements in manufacture and fabrication are constantly opening new possibilities to the phenolic trade. Mixtures of phenolic resins and vinyl resins have been used for the manufacture of phonograph records. A similar mixture containing 20–30% of rubber has been used as a molding composition. A mixture of viscose, phenolic resin, rubber, and sulfur can be molded and vulcanized. Phenol-formaldehyde resins have

been used successfully as substitutes for metal bearings. Recent developments include the formation of a water-soluble resin, made by means of an alkaline catalyst, which acts as a stabilizing agent for rubber latex; a cold-setting phenolic resin, made with an acid catalyst; a liquid resin which does not harden at normal temperatures, but which cures rapidly when heated. A recent development in the fabrication of phenol-formaldehyde resins consists of heating sheets of the cured resin to a temperature just below their decomposition point and then shaping them under pressure. The flat sheets and the shaped material produced by this process of post-forming phenolic resins are shown in Figure 10.5.

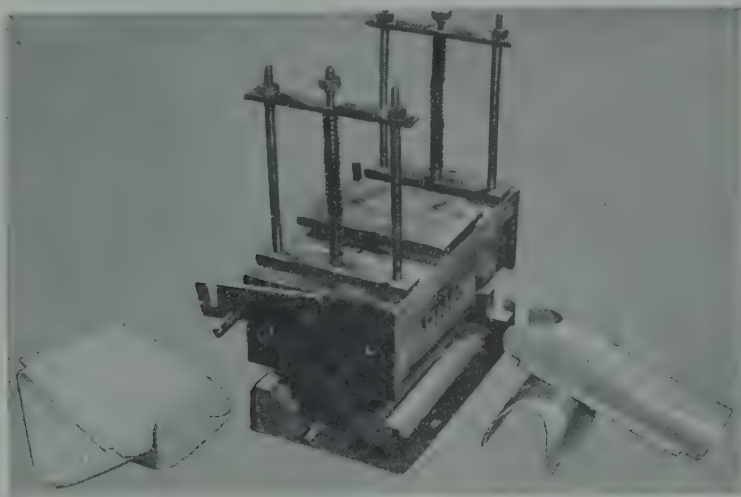


FIG. 10.5. Post-forming of phenolic sheets. (Courtesy of Formica Insulation Company.)

The molding compounds are sold in powdered or granular form ready for final processing. The phenolic resin base is also marketed in the form of ground resin (alone or mixed with "hexa"), as solutions, dispersions, or prefabricated sheets and stock shapes. A few trade names of phenol-formaldehyde resins are:³

Bakelite, Heresite, Makalot, Resinox, Durez, Durite, Indur, Nevillite, Textolite, Kellite, Neillite.

CAST PHENOLICS

Manufacture.—In the production of cast phenolics, the ratio of phenol (or other aromatic hydroxy compound) to formaldehyde is ad-

³ No attempt will be made in this book to list all of the trade names of a given type of plastic. For a comprehensive listing of the trade names, principal applications, and manufacturers of the various types of plastics, see Simonds and Ellis, *Handbook of Plastics*, pp. 991–1011, D. Van Nostrand Co., New York, 1943.

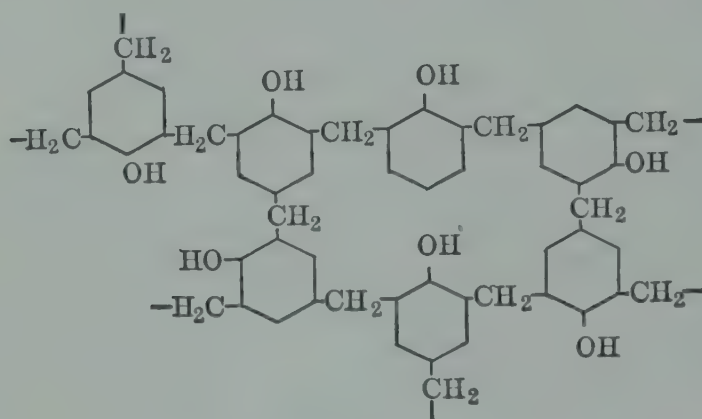
justed to provide an excess of formaldehyde during the process. Approximately 2.3 equivalents of formaldehyde are used for each equivalent of phenol. A caustic alkali such as potassium hydroxide or sodium hydroxide (15–30 g. of alkali for 1000 g. of phenol) is added to the reactants in a nickel-lined autoclave and the reaction is carried out at approximately 70° C., for 2.5–3 hours. Since the reaction is exothermic, rigid control of the temperature must be maintained. The phenol alcohols which are characteristic of the alkali-catalyzed reaction are formed in the initial stages and these, in turn, remain in the aqueous medium of the reaction. The conditions are adjusted so that no precipitation or deposition of the resin from the water solution will occur, even if the kettle is cooled to 10° C.

When the reaction has reached the desired degree of polymerization, dependent upon the properties of the casting desired, the solution is neutralized and then acidified with lactic acid. This acid is most suitable because sodium lactate is extremely soluble in water and hence stays in solution in the water remaining in the final product. Citric acid has a similar effect, but oxalic or tartaric acid produces a turbidity. Formic, acetic, and phthalic acids cause the formation of dark colored resins. The light straw-colored resin solution is then subjected to vacuum dehydration at 75°–85° C. until a water content of 5.0–9.0% has been reached. Mold lubricants, dyes, pigments, and glycerol are added and the viscous resin, which is really a hydrophilic sol, is poured into suitable lead, glass, or rubber molds. The addition of dimethylolurea at this stage gives rise to the formation of a phenol-formaldehyde, urea-formaldehyde copolymer product which possesses excellent colorability and translucency.

The liquid resin is converted slowly into the infusible, insoluble "C" stage by heating for 2–5 days at approximately 80° C. Large castings have been described in which the curing was accomplished by heating for 2 hours at 80–85° C. As the condensation polymerization which results in this change proceeds, the hydrophilic sol gradually changes into a soft and then a hard gel. The gelation is accompanied by deposition of the water content into fine droplets which are entrapped in the hardened structure. The function of the glycerol, which was added before the resin was poured into the mold, is to minimize the opaqueness of these water droplets. The cast product may be *case hardened* by removing it from the mold and heating it for 24–48 hours at 75–80° C., in order to drive all volatile matter—formaldehyde or moisture—from the surface. A practical application of case hardening is the manufacture of billiard balls from a cast phenolic resin containing an appreciable amount of water.

After curing, the product is heated to dehydrate and harden the outer surface. The performance of the billiard ball is explained by the hardness of the outer shell and the resiliency of the inner structure.

The unusual characteristics of cast phenolics—particularly factors of strength and colorability—may be explained from two viewpoints. First, the chemical structure of the *resol* type resin obtained under the conditions used involves a multiplicity of cross-linkages and a well-knit structure



Such a structure has long been associated with mechanical strength.

The second viewpoint, however, stresses the hydrophilic nature of the resinous product formed. The prolonged solubility of the resin in the aqueous phase of the reaction is in distinct contrast to the hydrophobic phenolic resins which separate as they are formed. As the hydrophilic sol gradually changes to a hydrophilic gel, therefore, the water remains as a true immobilized medium in the gel. The size of these droplets may be measured and compared with the total water content of the resin. See Table II-10. The physical

TABLE II-10^a

Water Content, Hydrophilic System Per cent	Particle Size, Microns
14.15	6.8
12.52	3.4
10.52	1.5-2
9.46	1.0-1.5
8.60	0.2-1.0

^a Plastics Catalog, p. 95, 1943 edition, published by Plastics Catalog Corporation, New York.

properties and particularly the color are determined by the amount of water present and the size of the droplets.

The two factors to which particular attention must be paid in the preparation of cast phenolics are, therefore, the water content and the viscosity. The former is the cause of such properties as high impact, flexural and tensile strengths, and degrees of opaqueness or translucency. It should be emphasized that the values of these properties are no better than those of filled, molded phenolic resins, but they are obtained without the benefit of any added filler. (See Table III-10, page 182.) The viscosity is of major importance in regulating the ease of flow into the molds and the time required to permit air bubbles to rise to the surface.

Recent developments in the casting of phenolic resins have indicated that many additional commercial products may be manufactured by this process as a result of faster curing techniques. The use of a strong acid, added immediately before curing, permits curing of the casting in two hours without the use of heat. The product thus obtained, however, has poorer strength and aging properties. Heating of the casting during cure reduces the shrinkage with age and thus improves dimensional stability. As a general rule, the faster the cure the greater will be the attendant shrinkage. Impact strength of cast phenolic products can be increased by the addition of fillers such as walnut shell flour and asbestos. With each of these fillers, however, dimensional stability, flexural, tensile, and compressive strengths are all decreased.

Properties and Applications.—When production demands favor the manufacture of small lots or when special designs which may be easily fabricated from stock sheets, rods, or tubes are desired, cast phenolics are often chosen in preference to molded phenolics. In numerous other cases, however, casting has arisen to a process of importance because of various desirable and otherwise unattainable properties. Cast phenolics are particularly noted for their colorability, strength, and machinability. With adequate control of the production of cast phenolics, artful and colorful designs may be created. By proper regulation of droplet size, translucency or opacity, with their resultant influence on the color produced, may be varied. This factor is directly opposite and in striking contrast to the poor colorability encountered in molded phenolics.

The role of the occluded water droplets in an explanation of the high tensile, flexural, and impact strengths exhibited by cast phenolics has been previously mentioned. Whether these properties are best explained on the basis of multiple cross-linkages or the hydrophilic

nature of the resin is of less commercial interest than the existence and value of such properties in numerous applications. As the comparison of cast and molded products is continued, it is noticeable that many features of the molded material also apply to the cast phenolics. The thermosetting nature of the resin used insures that after proper hardening, moderate heat-resistance, rigidity, and non-flammability will result. Although the temperatures at which the cast article may be safely used are not nearly as high as those for the molded product, this is probably due to the absence of filler in the cast phenolic resin and to the fact that a lower degree of polymerization is obtained. Cast phenolics are not generally used where elevated temperatures will be encountered. It is interesting to note, however, that more rapid curing methods, using a strong acid as the catalyst, will yield a product having improved heat resistance.

Although casting resins are more expensive than molding powders, the casting process itself is economical for two reasons. First, the molds used in the preparation are easily formed in any quantity. The lead molds are used only once, but the lead can be recovered easily and used for making new molds. Secondly, the ease of machining the cast phenolics makes them readily adaptable to a variety of uses which require only the standard sheet, rod, or tube shaped castings for their preparation. By such finishing operations as cutting, sawing, drilling, embossing, and polishing, even the more complex forms may often be fabricated. Figures 10.6 and 10.7 illustrate the turning and sawing of cast phenolic resins.

The combined features of relatively low cost and color retention make the cast phenolics competitive with all other types of fabricated plastics. The latter property particularly sets these materials apart from other phenolics. The availability and cost, on the other hand, leaves the cast phenolics in a field in which they can compete favorably with such colorable plastics as the ureas or acrylates. Common-place articles which may be manufactured from this base include:

- Clock cases
- Radio cases
- Instrument dials
- Dresser sets
- Grinding discs
- Translucent paneling
- Advertising displays
- Machine tool parts
- Jewelry, novelties
- Lighting fixtures.

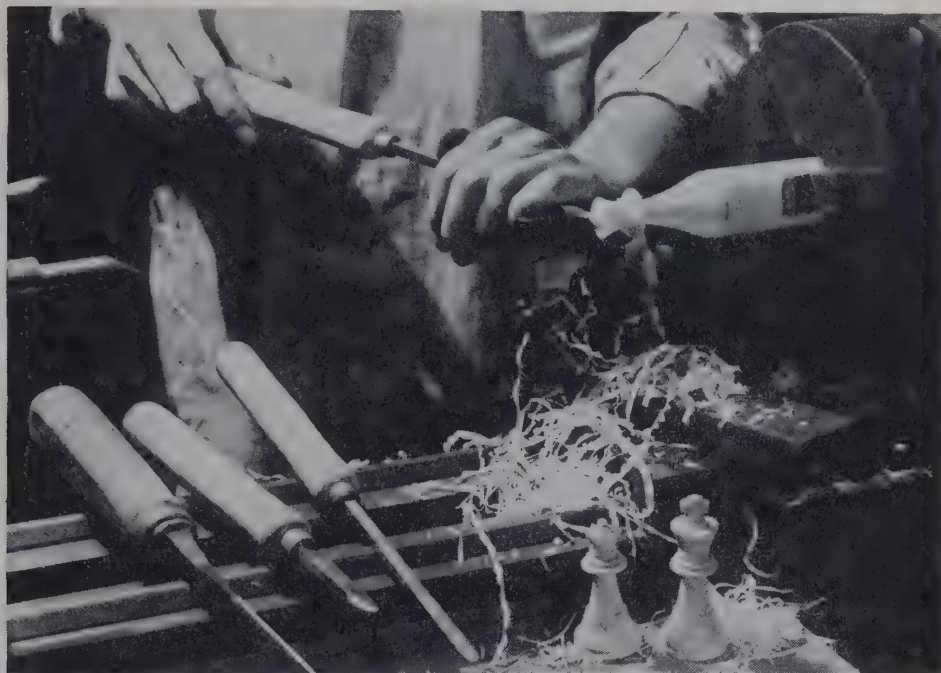


FIG. 10.6. Turning of cast phenolic resin. (Courtesy of Catalin Corporation.)

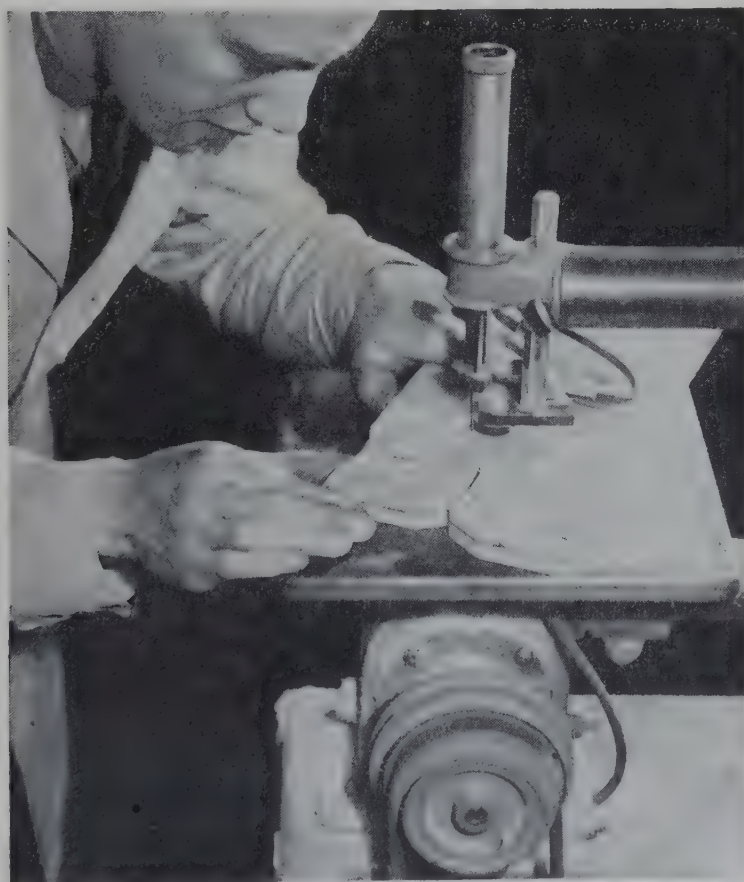


FIG. 10.7. Sawing cast phenolic resin. (Courtesy of Catalin Corporation.)

TABLE III-10. COMPARISON OF PHYSICAL PROPERTIES OF PHENOL-FORMALDEHYDE, UREA-FORMALDEHYDE
AND MELAMINE-FORMALDEHYDE RESINS^a

Properties	Phenol-Formaldehyde				Urea- Formaldehyde	Melamine- Formaldehyde
	Wood Flour Filled	Asbestos Filled	Fabric Filled	Cast		
Specific gravity	1.34-1.52	1.70-2.09	1.37-1.40	1.27-1.3	1.48	1.4-1.7
Tensile strength, lbs. per sq. in.	6,000-11,000	5,000-10,000	6,500-8,000	6,000-12,000	5,500-7,000	3,600-7,570
Modulus of elasticity, lbs. per sq. in. $\times 10^5$	10-15	10-45	7-12	5-15	12-15	12-15
Compressive strength, lbs. per sq. in.	16,000-36,000	18,000-36,000	20,000-32,000	15,000-30,000	20,000-24,000	—
Flexural strength, lbs. per sq. in.	8,000-15,000	8,000-20,000	10,000-13,000	10,000-14,000	10,000-14,000	10,000-19,000
Impact strength, ft. lbs. per inch of notch	.20-.56	.22-.72	.8-4.8	.35-	.28-.32	.28-.32
Brinell hardness, 25 kg.	30-45	—	32-40	30-45	48-54 (500 kg.)	—
Thermal conductivity, 10^{-4} cal. per sec. per cm. per °C.	4-12.2	8-20	3-5	3-5	7.1	—
Thermal expansion $\times 10^{-6}$ in. per in. of length per °C.	3.7-7.5	2.5-4.0	2.0-6.0	2.8	2.5-3.0	—
Safe top operating temperature °F.	300	400	250-350	160	175	210
Softening point	none	none	—	—	none	none
Distortion under heat °F.	> 275	—	250	> 160	260	266-410
Cold flow	none	none	< 1%	none	very low	none
Dielectric strength volts per mil	300-500	475	300-450	300-400	500-700	270-535
Power factor, 10^6 cycles	.035-.100	.005-.100	.04-.100	.01-.045	.03	.028-.038
Water absorption per cent by weight in 24 hours	.2-6	.01-.30	1.0-1.3	.01-.50	1.0-3.0	.2-6

^a A Ready Reference for Plastics, 1943 edition, Boonton Molding Company, Boonton, N. J.

Of widespread interest was a 9 ft. statue at the New York World's Fair made from a cast phenolic resin. The largest cast phenolic resin made to date is a trunion plate which measures 14 ft. \times 4 ft. \times 1 ft. and weighs 1,350 lbs.

The resins used for the casting operation and the finished cast products are manufactured under the following trade names:

Bakelite Cast Resinoid, Catalin, Opalon, Opalite, Prystal, Formalin, Gemstone, Marblette.

PHENOLIC RESINS FOR COATINGS

A principal application of phenolic resins is that of base materials in the coating industry. The principal phenols used in making resins for this purpose are phenol, cresol, xylenols, and para substituted phenols (*p*-phenyl, *p*-tert. butyl, *p*-tert. amyl etc.). The resins may be used alone or after modification with natural resins or oil-resin combinations. The many commercial products fall into one of two classes, non-heat convertible and heat-convertible.

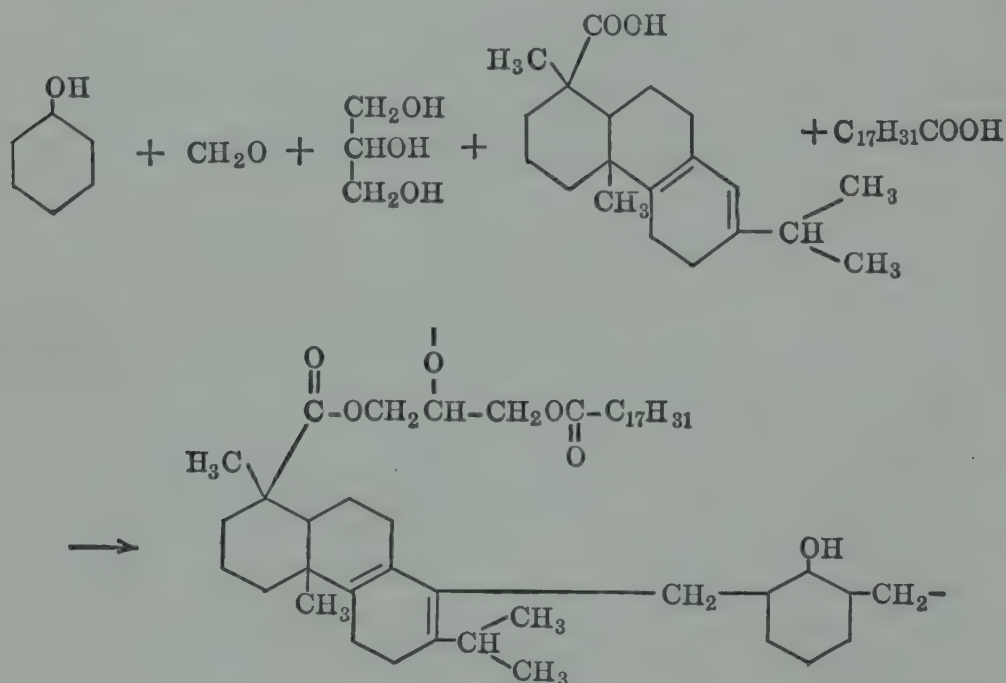
A. Non-heat Convertible Resins. This class includes those resins prepared with an insufficient amount of formaldehyde to produce complete hardening. They may be subdivided into two groups:

1. Alcohol-soluble
2. Oil-soluble (also includes stable homogeneous dispersions).

The alcohol-soluble class is limited in its application because of the absence of flexibility and toughness. Some use has been made of this type as a shellac substitute. When an ortho or para substituted phenol is used instead of phenol, an oil-soluble resin is obtained. This initial phenolic resinous product is dissolved by heating with the desired drying oils to 60–80° C. for 4–5 hours. Based upon changes in specific refraction and viscosities, there is some evidence of a chemical reaction between the resin and the drying oil, particularly if the drying oil has a conjugated system of double bonds. The exact nature of the chemical reaction is not yet known. Unmodified oil-soluble phenolics which enjoy such wide application in oleoresinous varnishes and enamels are thus formed. A typical formulation consists of two to three parts of oil combined with one part of resin. Linseed, dehydrated castor, soya, tung, and oiticica oils are representative of those used.

When further modification of the properties is desired, an oil-soluble modified phenolic may be produced by allowing either a substituted or an unsubstituted phenolic resin to react with a natural

resin (rosin, ester gum) and an oil. A synthetic resin, particularly one of the alkyd class (see p. 325), may be made from phenol, formaldehyde, glycerol, a rosin and an unsaturated carboxylic acid.



An oil modified phenolic may also be produced by condensing a phenolic resin with phthalic anhydride and castor oil at about 85° C. These modified resins produce "quick-drying" varnishes of desirable toughness and hardness.

B. Heat Convertible Resins. The same general types of mixtures may be prepared from a base resin which is capable of being hardened by heat alone. Many of the baking enamels of the coating industry are produced by the use of either an alcohol-soluble or an oil-soluble hardenable phenolic resin. The alcohol-soluble type consists of the resin used without modification for coatings of exceptional hardness, resistance to moisture, insolubility in solvents, and resistance to corrosion. Low flexibility limits their use.

When this basic resin is modified by treatments with a natural resin and a drying oil, or either alone, the oil-soluble type is formed. Excellent durability, water resistance and hardness are characteristics of this class.

PHENOLIC-ASBESTOS COMPOSITION

A phenolic-asbestos composition, particularly recommended for its chemical inertness and resistance, is sold under the trade name,

Haveg. Special types are advised according to the specific kind of resistance desired, but all are based upon modification of a casting type of phenolic resin with asbestos as filler. Graphite is used in place of asbestos where resistance to hydrofluoric acid is desired (*Haveg* 43).

Large castings such as tanks, (Figure 10.8), vats or tubing may be prepared from the most suitable type in much the same way that comparable units might be fabricated from cement or concrete. Although a fundamental constructional material, however, reinforcement of *Haveg* by supporting metal or wooden members is often advisable. Digestion tanks, filters, pipe fittings, valves and pickling tanks are representative of the type of product which may be fabricated from this material.



FIG. 10.8. *Haveg* tanks used in chemical operations involving corrosive acids. (Courtesy of *Haveg* Corporation.)

Haveg 41 is resistant to practically all inorganic acids except oxidizing acids, to most salts, weak bases, chlorine, and many organic solvents.

Haveg 43 contains a carbonaceous filler and is resistant to hydrofluoric acid.

Haveg 50 is resistant to strong bases and most inorganic acids.

PHENOLICS IN LAMINATING AND BONDING

Phenolics are applied in the formation of lamination products to be used for industrial and decorative purposes. Since the laminate consists fundamentally of paper or fabric sheets impregnated with

resin, cut to proper dimensions, and molded by pressure to the desired shape, it is to be expected that the properties of the product are dependent upon the grade and type of sheet stock used and upon the resin applied. The types of fillers and the properties imparted by each were discussed on p. 173.

The phenolic resins applied to this fabrication method are prepared by the one-step process according to the same general methods applied to the formation of the casting resin. The reaction, however, is carried to the point at which a solid resin forms when cooled. The resin is compounded into a varnish by adding alcohol or a mixture of alcohol and water as the solvent, followed by addition of plasticizers, lubricant, and dye as desired. Since the resins are of the thermosetting type, heat must be applied during the curing process. The product obtained is infusible and insoluble. It exhibits excellent mechanical strength, light weight, chemical resistance, and high dielectric strength. One of the primary factors explaining its widespread use is the ease of machining the laminated stock sheets, rods, or tubes obtained by molding. They may be punched, drilled, sawed, threaded, or milled with little difficulty.

The uses of laminated products are widespread. Their application and value as gears, pulleys, cams, housings, insulation, electrical coil forms, tubing for chemical equipment, and propeller supports have been proved in industry. Asbestos shingles are shaped in molds constructed of laminated phenolics. Fluorescent and luminescent signs, signals, and decorative effects are manufactured from laminated materials. X-ray equipment is frequently made from laminated phenolics because of their excellent mechanical strength, high dielectric strength, and the distinguished appearance of the product. In this application, resistance to x-radiation is produced by the addition of oxides or salts of high atomic weight metals. An outstanding feature of laminated gears is the fact that they are lubricated by water (in direct contrast to metals) and only slightly affected, if at all, by the presence of injurious acids, salts, or alkalies.

The use of phenolics in bonding applications is exemplified by their use in plywood construction. Since bonding is discussed in Chapter XXIV it is sufficient to state here that the composition of the phenolics may be adjusted to produce either a cold-set or hot-set adhesive. In both cases, heat and pressure are applied to effect final cure, but in the case of cold bonding the term merely refers to the fact that heat and pressure are not applied simultaneously. New advances in phenolic resins have introduced the possibility of using

a powdered resin which is soluble in water at temperatures of 110–150° C., and which becomes water-resistant after curing.

PHENOLIC RESIN BOARD

A pre-fabrication form of phenolic resin known as phenolic board or blanks is produced by simultaneous deposition of resin and fiber into a mat on a typical paper-making machine. In this way, the resin and fiber are intimately mixed and unusually high impact-strength products may be fabricated simply by heating in a suitable mold. Any desired shape may be punched from the continuous board produced and these, in turn, may be molded to the usual thermoset, rigid form. The low bulk-ratio of the board to the finished article combined with the excellent mechanical properties which may be so produced make this product industrially valuable.

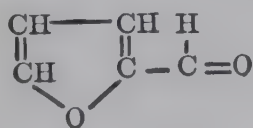
PHENOLIC SISAL PLASTICS

A sisal fiber matting impregnated with phenolic resin is sold under the trade names Co-Ro-Lite and Co-Ro-Felt. Actually, the product consists of a sisal matting which resembles a "felt-like blanket." The resin in either solution or powdered form is thoroughly incorporated into the mat and the polymerization is advanced to the point where it is ready for molding. Moldings, usually of a simple nature such as trays or abrasive discs, may be formed. Excellent impact strengths result and high tensile and flexural values are retained.

PHENOL-FURFURAL RESINS

The chemistry of the preparation and fabrication of the resinous products prepared from combinations of phenol and furfural is in most respects similar to that involved in the production of phenol-formaldehyde resins. The reaction of aldehydes with phenol or other hydroxy aromatic compounds is not limited, therefore, to formaldehyde. Other saturated aliphatic aldehydes in combinations with phenol have been investigated. No commercial product was produced from such a similar reaction, however, until furfural was obtained as a by-product from grain.

Although there is general similarity between the formaldehyde and furfural reactions with phenol, they differ in certain respects. The formula for furfural shows that the molecule contains not only an aldehyde group, but also two double bonds.



During the course of the reaction with phenol, it behaves as a saturated aldehyde until the final stages of gelation and curing are reached, when cross-polymerization accompanied by the disappearance of double bonds occurs. The final structure of well-knit, interlaced molecular chains is thus formed.

The usual reaction is conducted under conditions of alkaline catalysis followed by compounding to either molding or laminating formulations as in the case of the formaldehyde derivatives. The greatest observable difference during the reaction is that there is no gradual transition through *A*, *B*, and *C* stages in this case. Gelation or partial hardening is evidently hindered by the presence of a ring structure in the aldehyde molecule. As a consequence, the phenol-furfural resins undergo a very sharp transition from the plastic, softened state to the cured, infusible state.

The furfural resins are also comparable to the phenol-formaldehyde resins with respect to physical properties. The greater degree of interdependency caused by the interlaced cross-linkages of the furfural derivative, however, produces exceptional values of impact and tensile strengths when properly cured. Since such properties are dependent upon changes in compounding, comparisons are sometimes difficult. The fillers and plasticizers found to be desirable in the fabrication of the phenol-formaldehyde resins are also suitable for phenol-furfuraldehyde resins. Slight superiority over the common phenolics in electrical characteristics is also encountered in the furfurals. Low arc resistance is, however, associated with both.

The particular property of the furfural resin which is of foremost industrial importance is its behavior at high temperatures. Interesting characteristics are exhibited by both the unmolded and the cured materials. First, the unmolded, uncured material, as mentioned previously, has little tendency to gel before the actual curing conditions are reached. Samples of the unhardened product may be maintained for considerable periods just below the molding temperatures without appreciable hardening. This feature permits the use of phenol-furfural resins in the injection-molding process. The material has been successfully handled by pre-softening in a heating chamber until complete plasticization has occurred before injecting it into a mold heated to a higher temperature. At this higher temperature, cure proceeds very rapidly and the molded product may be ejected from the hot mold. Successful injection molded products have been formed in this way. Secondly, the finished article is resistant to the continuous application of temperatures 10–20° C. higher than those recommended for phenol-formaldehyde resins. Thus, although

more elevated temperatures with their attendant difficulties are necessary for the curing of phenol-furfural resins, the results often warrant their use. The difference between the formaldehyde and furfural derivatives when heat is applied has led to the use of a combination of these two resins for regulation of flow. Restricted flow may thus be obtained. Such a product is useful in the impregnation of an open, porous material.

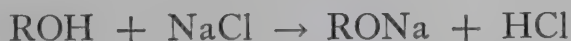
Other properties such as chemical inertness, poor colorability, dimensional stability and general adaptability are common to both the formaldehyde and furfural derivatives.

The phenol-furfural resins are particularly noted for the wide choice of fabrication methods which are possible. Compression, injection and transfer molding; laminating, abrasive wheel castings, varnish or adhesive formulations may all involve this type of resin. Such widely diversified products as electrical switches, automotive parts, machine housings, filing cabinets, or utensil parts are manufactured from this base product.

This type of resin is sold under the trade-name Durite in the form of molding compounds, liquid and powdered resins.

ION-EXCHANGE RESINS

A very interesting application⁴ of phenol-formaldehyde and related resins is that of "ion-exchange." It is evident from the formula of phenol-formaldehyde resins given on p. 165 that the phenolic hydroxyl group is not affected by the condensation reaction of phenol and formaldehyde. Consequently, a phenol-formaldehyde resin may be pictured as a large, insoluble molecule having many phenolic hydroxyl groups capable of reacting with water-soluble salts. If a dilute solution of sodium chloride is passed through a column packed with properly sized granules of such a resin, the following reaction occurs:



where ROH represents a portion of the phenol-formaldehyde resin. The effluent liquid consists of a dilute solution of hydrochloric acid. Increased exchange capacity, especially for salt solutions having a low pH value, can be obtained by substituting a phenol sulfonic acid for part of the phenol in the original condensation with formaldehyde. Another method of introducing sulfonic acid groups is to allow a phenolic resin, which contains some reactive hydrogen atoms, to react with formaldehyde and sodium sulfite. In this way methylene

⁴ Myers, Eastes and Myers, *Ind. Eng. Chem.* 33, 697 (1941).

sulfonic acid groups become attached to the aromatic rings. The "exhausted" resin, resulting from the ion exchange, may be regenerated by treatment with dilute sulfuric acid or dilute hydrochloric acid.

The acid in the aqueous solution emerging from the phenol-formaldehyde resin may be removed by passing the solution through an amine-formaldehyde resin. These resins may be made from the reaction of aromatic amines, e.g., aniline, *m*-phenylene diamine, with aldehydes such as formaldehyde or a monosaccharide. Although the aldehydes react with the amine groups as well as the ortho and para hydrogen atoms, there are still some free amine groups to react with the aqueous solution of acid, e.g.,



where RNH_2 represents a portion of the amine-aldehyde resin. The acid absorption capacity can be increased by adding alkyl halides to the reaction mixture in which the resin is being made in order to form quaternary ammonium salts which on treatment with alkali will yield quaternary ammonium bases as parts of the insoluble resin. An "exhausted" amine-aldehyde resin can be regenerated by treatment with alkali. By passing a dilute salt solution first through a cation-exchange resin and then through an acid-absorbent resin, it is possible to obtain water which compares very favorably with distilled water.

Review Questions

1. Show by chemical reactions the formation of: (a) Novolak and (b) resol type resins.
2. How does the addition of (a) *o*-cresol, (b) *m*-cresol, (c) *p*-cresol, (d) *p*-alkylphenol, (e) 2,4-xyleneol, (f) 3,5-xyleneol in place of phenol, affect the properties of the polymer?
3. Why is "hexa" used in the molding of a two-stage phenolic?
4. What properties are characteristic of the molded phenolics?
5. Why are para-substituted phenolics often used in formulating coatings?
6. What are each of the following: (a) Havel, (b) Co-Ro-Lite, and (c) Durite?
Mention one outstanding property and application of each.
7. How does the chemical reaction between furfural and phenol differ from that between phenol and formaldehyde?
8. Describe the preparation of a casting phenolic resin.
9. What is the importance of the water content in a cast phenolic resin?
10. Compare the properties of a cast and molded product.

CHAPTER XI

SYNTHETIC PLASTICS II: AMINO ALDEHYDE RESINS

Although the general phenol-formaldehyde molding powders are suitable for many uses, manufacturers recognized the limitations of their poor colorability early in the history of their development. Resins prepared from urea and formaldehyde were introduced into industrial fabrication processes because of this need for a colorable thermosetting material. It is true that cellulose acetate plastic products were popular in a wide range of colors and design before the urea-formaldehyde resins were first marketed in 1928. The combination of the two properties, heat hardenable and colorable, however, was not present in any resin previous to the urea-formaldehyde resins. They were introduced, as a matter of fact, through the efforts of the Toledo Scales Company to obtain a colorable phenolic-like resin which might be used in their product.

The reaction of urea with formaldehyde, and the accompanying formation of a resinous product, was investigated as early as 1897. Lack of interest in such products at that time prevented industrial exploitation. About 1920, an inexpensive method of making urea was developed by the I. G. Farbenindustrie, and, soon after, the industrial possibilities of the resinous products obtained from it became apparent. At present, urea is prepared by the interaction of ammonia and carbon dioxide. The ammonia used may be obtained (1) from the combination of nitrogen with hydrogen, (2) from calcium cyanamide treated with hot water, or (3) as a by-product from the destructive distillation of coal.

Manufacture.—The manufacture of urea-formaldehyde resins may be carried out in a variety of ways with many accompanying changes in the properties of the product. For example, any of the following factors may be altered in the preparation of specific types of resins:

1. Use of either an alkaline or acidic catalyst.
2. Regulation of temperature and pressure.
3. Concentrations of both urea and formaldehyde in aqueous solution.
4. Method of addition—urea to formaldehyde or vice versa.
5. Ratio of formaldehyde to urea.

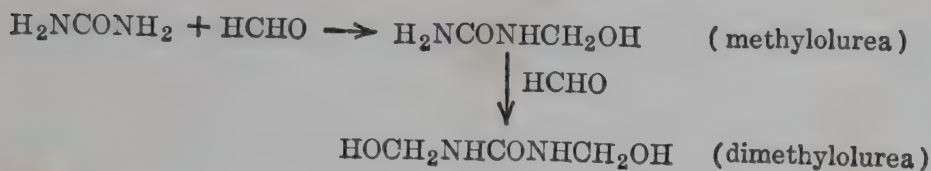
The usual process which results in the formation of a molding powder involves a reaction carried out under the influence of an alkaline catalyst during the initial stages. Aqueous solutions of urea and formaldehyde are mixed in the reaction kettle, together with an alkaline catalyst such as calcium hydroxide or ammonia. An acidic catalyst may be used even at the beginning of the reaction, but under these conditions control is most difficult. If the reaction becomes too vigorous, a porous mass may be formed.

During the initial stages, the reaction results in the formation of products which remain water soluble. For the first two hours, the mixture is allowed to stand at room temperature. This results in the formation of an A-stage resin consisting mainly of the condensation products, mono- and di-methylol ureas. This solution is then heated to boiling until it becomes a viscous, syrupy mass. Dehydration by vacuum drying at 85–90° C. leads to the formation of the solid resin. Before the resin is finally cured in the molding process, the alkaline catalyst is replaced with an acidic catalyst.

In the commercial production of urea-formaldehyde resins the molar ratio of formaldehyde to urea is usually 1.5–2.0:1. A higher proportion of formaldehyde produces harder resins at low pH, probably as a result of an increased number of cross-linkages. However, larger amounts of formaldehyde may cause cracking or crazing of the molded product on aging.

A patented method of producing a urea-formaldehyde molding powder involves the reaction of 1.3 moles of urea with 2 moles of formaldehyde in a neutral or slightly acidic medium at 80–90° C. until a small increase in viscosity occurs. Dehydration by vacuum at a low temperature results in a dry hydrophilic resin which may be compounded with cellulosic filler, lubricant, hardening agents, and dyes for a molding powder. It has been found that ratios of less than 1 mole of urea to 2 moles of formaldehyde result in poor hardening action at pH of 5.5 or above, and hardening followed by shrinking and cracking when aged at pH lower than 5.5. When the amount of urea is increased to 1.1–1.3 moles, however, the reaction nears completion even at pH of 7.

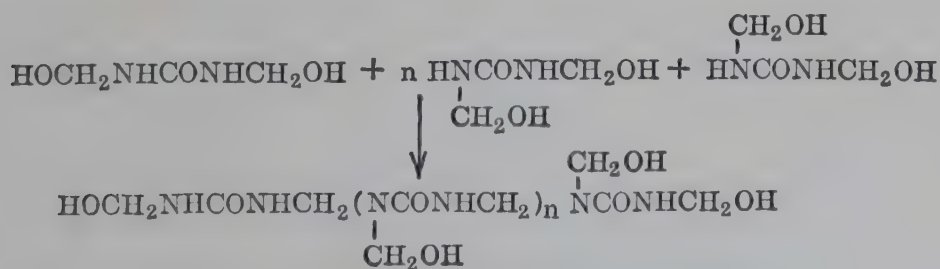
Although it is theoretically possible for one mole of urea to react with four moles of formaldehyde, the only simple products which have been isolated from the interaction of urea and formaldehyde are methylolurea and dimethylolurea.



One mechanism which has been proposed to account for the polymerization of methylolurea and dimethylolurea is to assume that they are first dehydrated to form methyleneurea ($\text{H}_2\text{NCON}=\text{CH}_2$) and dimethyleneurea ($\text{H}_2\text{C}=\text{NCON}=\text{CH}_2$). These unsaturated compounds could then polymerize by an addition mechanism. The presence of two unsaturated linkages in dimethyleneurea would cause the formation of cross-linkages. In picturing such a mechanism, the reaction may be described as occurring in four steps. These are:

1. *Addition*: resulting in formation of the methylolureas. This change is accelerated by heat and an acidic medium.
2. *Condensation*: the loss of water from methylolureas produces methyleneureas during this stage.
3. *Polymerization*: self-addition of methyleneureas results in the desired product. This hardening stage is greatly accelerated by acids or acidic salts, such as ammonium chloride. The action, on the other hand, is delayed by salts of alkali metals with weak acids.
4. *Hardening*: formation of cross-linkages.

A more probable mechanism involves the self-condensation of molecules of methylolurea or dimethylolurea. Methylolurea alone would be expected to yield only linear polymers, while dimethylolurea is capable of forming both linear and cross-linked polymers. Although the mechanism of the polymerization is not definitely known, it is reasonable to assume that the water-soluble polymers and the molding resins are linear polymers. When the compounded molding powder is heated, cross-linking occurs. The formation of a linear polymer from dimethylolurea may be represented as follows:



MOLDING POWDERS

After the polymerization has reached the stage where a resin suitable for use in molding powders has been formed, the reaction product is partially dehydrated. When alpha cellulose is used as a filler, and it is the most widely used filler for urea-formaldehyde resins, it is added to the liquid resin which still contains some water. This mixing is done in Monel metal, nickel lined or chromium plated mixing machines. More thorough drying in a vacuum oven may then be followed by incorporation of an acidic catalyst (oxalic acid, sodium sulfite, tartaric acid), additional urea or thiourea, a retardant (if necessary), pigments, plasticizers, and lubricants. The functions of these ingredients of the molding powder will be discussed.

Alpha Cellulose.—The common filler in urea-formaldehyde molding compositions is alpha cellulose because the desirable characteristics of translucency (see Figure 11.1) and colorability are thus maintained. Without the presence of such a filler, excessive shrinkage in the mold and undesirable aging characteristics would result. The particular effects of this filler are often ascribed to a chemical union between the filler and the resin, but this has not been confirmed.

The compounding possibilities are not limited to alpha cellulose, however. Wood-flour, lignin-enriched fabric, horn meal, and cotton flock have been successfully applied. Novel types of fillers include the reaction product of soybean meal and formaldehyde, or ground waste obtained from the molding of a typical phenol-formaldehyde resin. Amounts varying from 20–50% of any of these fillers may be

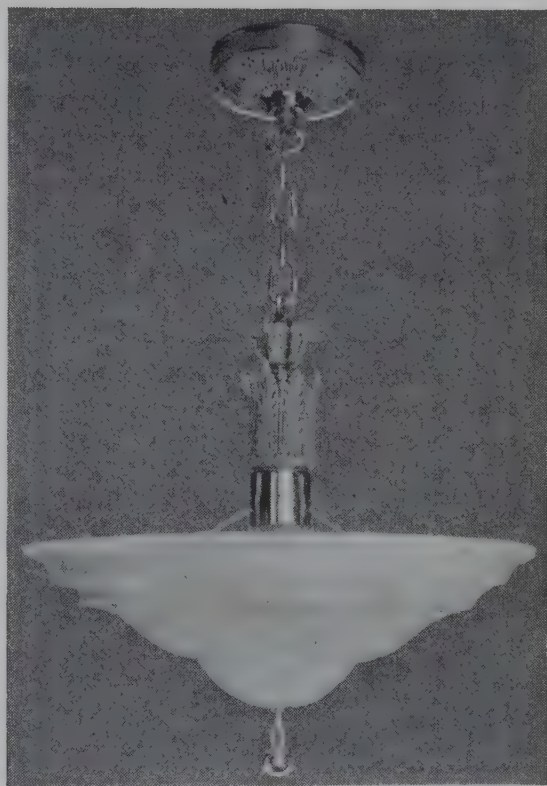
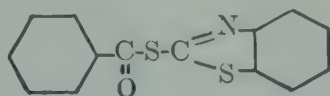


FIG. 11.1. Urea-formaldehyde resins with alpha cellulose as the filler are widely used in the manufacture of light reflectors and lamp shades. (Courtesy of American Cyanamid Company, Plastics Division.)

used by mixing with the syrupy resin at 30–40° C., followed by drying at 85–90° C. under controlled conditions of time and temperature.

Acidic Catalyst.—This ingredient catalyzes the final conversion from the initial stages of resin formation to the infusible, insoluble product. Two types of acidic materials are used. They are known respectively as *direct* and *latent* catalysts. The former are true acids and are, therefore, more or less effective at all temperatures. The latent catalysts are compounds which form acidic products at elevated temperatures. These, then, act as catalysts only above a minimum temperature. The list of possibilities in both classes is lengthy. Typical inorganic or organic acids, acid salts such as sodium acid sulfate or aniline hydrochloride, and organic esters typified by acid alkyl phosphates (alkyl group containing more than three carbon atoms) may be used as direct catalysts. A novel method of catalysis involving the use of a chlorinated aldehyde or a halogenated acylated urea during polymerization has been described in the literature. When such a reactant as chloral or chloroacetyl urea is used to the extent of approximately 0.25 mole during the latter stages of polymerization, a self-hardening molding powder may be formed directly. The latent catalysts are typified by sodium sulfite and benzoyl or phthaloyl mercaptobenzothiazole.



benzoyl mercaptobenzothiazole

Additional Urea.—To prevent the excessive shrinking and cracking which might result if excess formaldehyde remains in the molding powder, urea or thiourea is often added to combine with it.

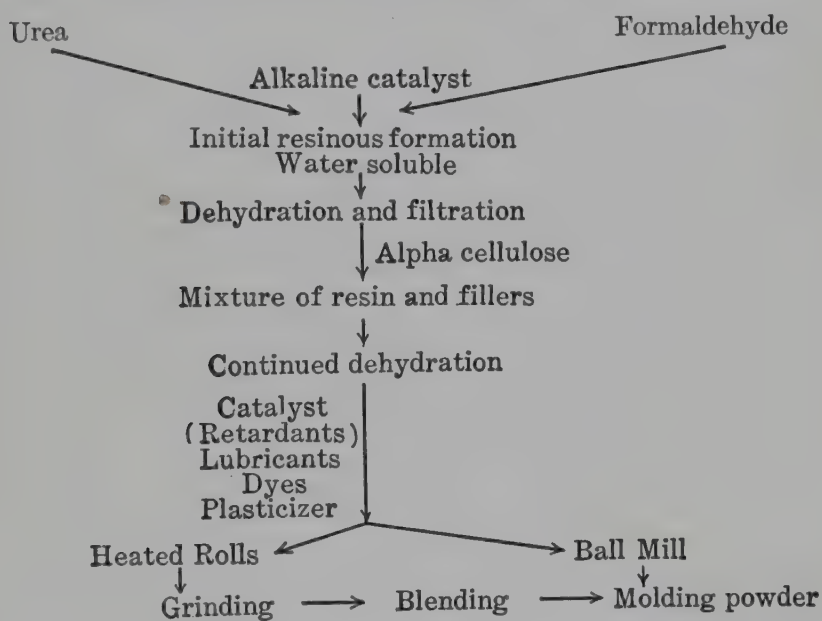
Retardants.—In cases requiring a long flow period in the mold or retarded action of final polymerization, lime, sodium carbonate, or salts of alkali metals with weak acids may act as efficient retardants. In large or intricate moldings this action is often necessary. The increased flow may often be obtained by the use of a suitable plasticizer. Triphenyl phosphate or a glyceryl phthalate resin (60 parts by weight per 240 parts by weight of urea-formaldehyde resin) have been suggested.

In the manufacture of molding powder, the final mixing operation in either a ball mill or on heated rolls involves further polymerization of the resin. In the presence of the acidic catalyst, the resin is more completely converted to a hydrophobic gel. This change is char-

acteristic of the conversion of the resin from the water soluble state to a water-insoluble, but still fusible polymer. With evidence of gel formation, the final dehydration may be completed. After grinding, screening and blending together several different batches to eliminate variations, the molding powder is ready for application.

TABLE I-11.

MANUFACTURE OF UREA-FORMALDEHYDE RESINS



Adhesives and Surface Coatings.—Urea-formaldehyde resins are widely used as adhesives, chiefly in the bonding of wood veneer into plywood. They are also used as surface coatings either in plasticized form alone or modified by other resinous types. When used as an adhesive the resinous base is prepared in a form which does not contain any cross-linkages and which may be converted to the permanently infusible form by proper treatment during bonding. The major fields of importance for this type of adhesive are in the fields of plywood construction and for the lamination of fabric. Urea adhesives are used for both purposes: in plywood for such purposes as the manufacture of decorative paneling, automotive parts, and boats; in laminating for table tops, light reflectors and soda-fountain bars.

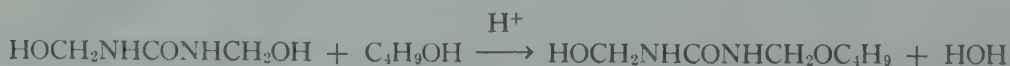
The resin used in such preparations is formed by the same general techniques outlined above. Much difficulty has been experienced in stabilizing the resin or its aqueous solution during storage and shipment. As a consequence, several improved methods have been suggested. The use of a volatile acid such as formic acid as the

catalyst for the preparation has been suggested. Volatilization of the catalyst then improves the stability. Also, a method which involves the addition of ammonia to the resin solution in order to fix the remaining formaldehyde has been proposed. The solution so obtained is stable, but addition of an acidic catalyst followed by deposition of the film results in loss of ammonia and the completion of hardening. The stable adhesive solution produced from urea and formaldehyde by tested, controlled methods may be used by either a hot-set or a cold-set technique.

The heat-setting adhesive becomes effective after the addition of an acidic hardening catalyst of the type outlined in the discussion of molding powders. Approximately 3–5% of catalyst may be added to the resin, and hardening, as in plywood construction, may be achieved by curing at 115–125° C. for 2–10 minutes at a pressure of 1000–2000 lbs. per sq. in. The working life of the mixed adhesive is about 24 hours. If it is desired to extend the adhesive, flour may be added without dangerously impairing the bonding. The cold-setting adhesive is marketed in two parts. The resin and hardener (often mixed with excess formaldehyde) are packaged separately. The two parts are mixed immediately prior to use (life of mixed adhesive 4 hours) and bonding may best be completed by application followed by heating at 50–95° C. and under pressure of 150–300 lbs. per sq. in. A waterproof bond is claimed, provided sufficient time is allowed to elapse and provided the humidity content of the woods being bonded is controlled to 5–12%.

An alternative to this method of formulating a cold-setting adhesive is the use of dried, ground resin mixed with dried powdered catalyst. When water is added to the mixture of solids the acid catalyst dissolves and exerts its effect on the water-soluble resin, thus causing the final action of hardening.

The characteristic of adhesiveness is also necessary in surface coating formulations. Urea-formaldehyde coatings may be applied either from aqueous or organic solvent media. Finishes which harden when subjected to heat, i.e., *baking enamels or varnishes*, are the most popular of the urea-formaldehyde surface coatings. The principal problem encountered in the preparation of these resins for coatings is adjustment of the conditions so as to obtain a product which is soluble in organic solvents. One method of accomplishing this is to treat dimethylolurea with butanol in an acidic medium to form a monobutyl ether of dimethylolurea.



This reaction is carried out under such conditions that a minimum of polymerization occurs. Xylene is then added and a mixture of xylene and water is distilled to dehydrate and concentrate the solution. The resulting butanol-xylene solution contains 40–60% of solid material. Polymerization occurs when the coating is baked. The intermediate resins may be compounded with alkyd resins, ethyl cellulose, or nitrocellulose. The urea-formaldehyde forms a hard, colorless non-yellowing film which is highly resistant to most solvents. When added to alkyds, a heat-reactive type of alkyd is generally used, for the ureas are of little value in the air drying types of coatings. The alkyds may be added to the prepared resin or a polybasic acid and polyhydric alcohol may be added to the reaction mixture and polymerization of both may proceed simultaneously. The presence of a polyhydric alcohol (glycerol) aids non-aqueous solvent solubility.

The particular advantages gained by compounding with alkyds are that the ureas harden the alkyds and make them more resistant to solvents. At the same time, the alkyds plasticize the urea resin. Commonly, heat curing of the films may be completed by baking for one hour at 125–150° C., but some types, involving the use of such acidic catalysts as mono- and di-esters of phosphoric acid, may be cured at as low a temperature as 50° C.

Casting.—Fabrication of a urea-formaldehyde resin by a casting procedure is not of general application because of the excessive shrinkage during curing, and the poor aging characteristics of the product. This method of processing may be applied, however, if conditions are properly regulated.¹ The initial stage of the resin formation is completed by condensing 1.3 moles of urea with 2 moles of formaldehyde in a slightly acidic medium until a slight change in viscosity is noted. The solution is then evaporated at low temperatures and decreased acidity. The casting molds may be filled with the viscous resin regulated to a pH of 5.5 to 6.5. These values are set as a maximum acidity at which bubbles are not occluded and a minimum value for a practical rate of hardening. The addition of plasticizing or softening agents (glycerol, castor oil) during the curing stage (60–80° C. for two days) reduces the shrinkage.

Properties and Applications.—The valuable and limiting properties of the urea-formaldehyde plastics may be discussed from both a general viewpoint and from the basis of factors evident only in specialized applications. Foremost in any consideration of these resins is the property of colorability. The rise and development of

¹ Smidth, U. S. Patent 2,174,535 (1939).

this resinous type is due almost entirely to the wide range of decorative effects possible with it. Almost all colors are equally stable and lasting; translucent or even transparent pieces may be produced.

Since urea-formaldehyde thermosetting resins were developed largely because of their greater colorability, as compared with phenol-formaldehyde resins, it is interesting to note the colorability of various plastics which are available for decorative purposes. This comparison is found in Table II-11.

TABLE II-11. PLASTICS AVAILABLE FOR DECORATIVE PURPOSES ^a

Substance	Color Selection
Molded phenolic plastics	Limited to darker opaque colors
Laminated phenolic plastics	Limited to darker opaque colors
Cast phenolic plastics	Unlimited
Molded urea plastics	Unlimited
Laminated urea plastics	Unlimited
Molded cellulose derivatives *	Unlimited
Laminated woven veneer †	Limited to veneer colorings
Sheets cellulose acetate	Unlimited
Casein plastics	Unlimited
Vinyl, acrylic, polystyrene resins	Unlimited

* Cellulose derivatives include nitrates, acetates, cellulose ethers, and mixed esters. Cellulose acetates predominate.

† Laminated woven veneers constitute strips of thin wood veneers woven into attractive patterns and bonded together by synthetic resin and pressed together under heat and pressure.

^a Del Monte, *Plastics in Engineering*, p. 462, Penton Publishing Company, Cleveland, 1942.

Even when combined with alpha cellulose, the glass-like character is retained and good translucency results. The characteristic of colorability introduces many difficulties into the molding procedure. Extreme caution must be taken to eliminate all dust and dirt from the molds or molding powder. The necessity of absolute cleanliness during the molding operation is evident from the applications shown in Figure 11.2. Traces of mechanical impurities, of course, mar the surface. For this reason, the preparation, storage and use of the powder must be carefully controlled. Separate machines and even separate molding rooms are set aside for the use of urea-formaldehyde resins.

Added to this molding-powder difficulty is the tendency of many molding powders to absorb moisture while in storage. The resinous

bases are water sensitive to a degree directly dependent upon the polymerization stage. The powder must often be dried in a pre-heating operation before actual molding. Then, too, the moisture

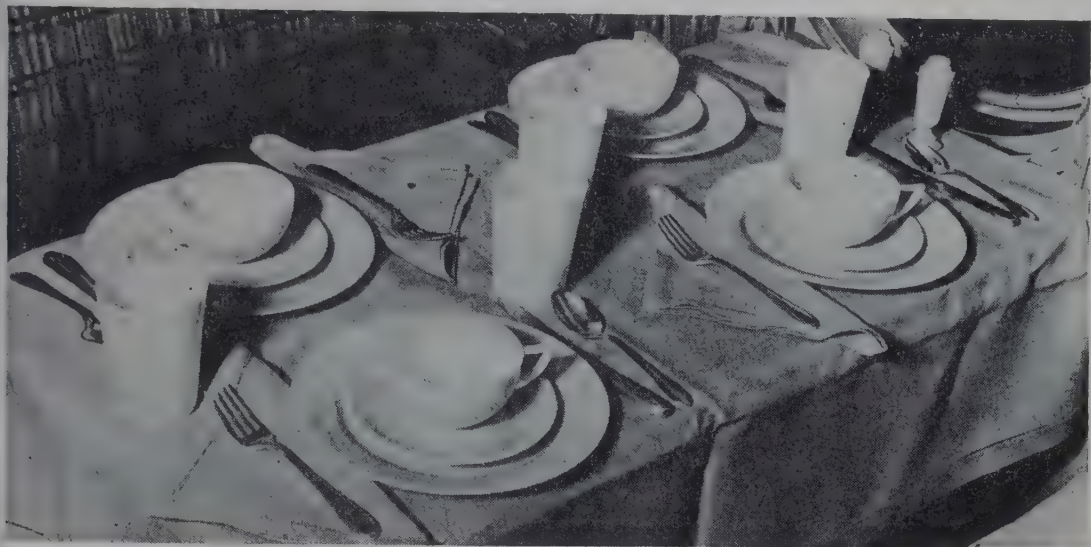


FIG. 11.2. Tableware molded from urea-formaldehyde resin. (Courtesy of American Cyanamid Company, Plastics Division.)

resistance of the finished article is necessarily poor because of the presence of the cellulosic filler. A fibrous filler of any type is likely to raise the water absorption. The urea-formaldehyde resins change their water content according to the humidity of the atmosphere with which they are in contact. The *breathing* of ureas is the loss and gain of moisture with changes in the humidity. This action may eventually result in cracking, warping, or distortion. Thus, values as high as 3% water absorption in 24 hours' immersion are encountered. Conversely, resins containing less alpha cellulose, or a different filler, or resins which have polymerized to a greater extent, show water-absorption values as low as 1%.

The heat resistance of the urea-formaldehyde resins is much lower than that of the thermoset phenolics. Use of these resins above 75° C. in a continuous operation is not recommended. Temperatures as high as 115° C. may be applied for short periods without particular damage, but over a long period of time discoloration and decomposition of the resin results. The absence of asbestos filler reduces the heat resistance of urea-formaldehyde resins as compared with the phenolics. The presence of asbestos in a urea-formaldehyde resin destroys its colorability.

Many of the applications in which the ureas may be found involve the ability of these resins to act as light diffusing bodies. Light may be transmitted through a urea-formaldehyde laminated panel, for example, without appreciable glare. In the manufacture of lighting fixtures and decorative paneling, diffusion of light without glare is often of primary importance. No other resin is as suitable for this effect. Unique designs are possible by variation of the film thickness through which the light passes or by printing colored sections on the urea-resin base.

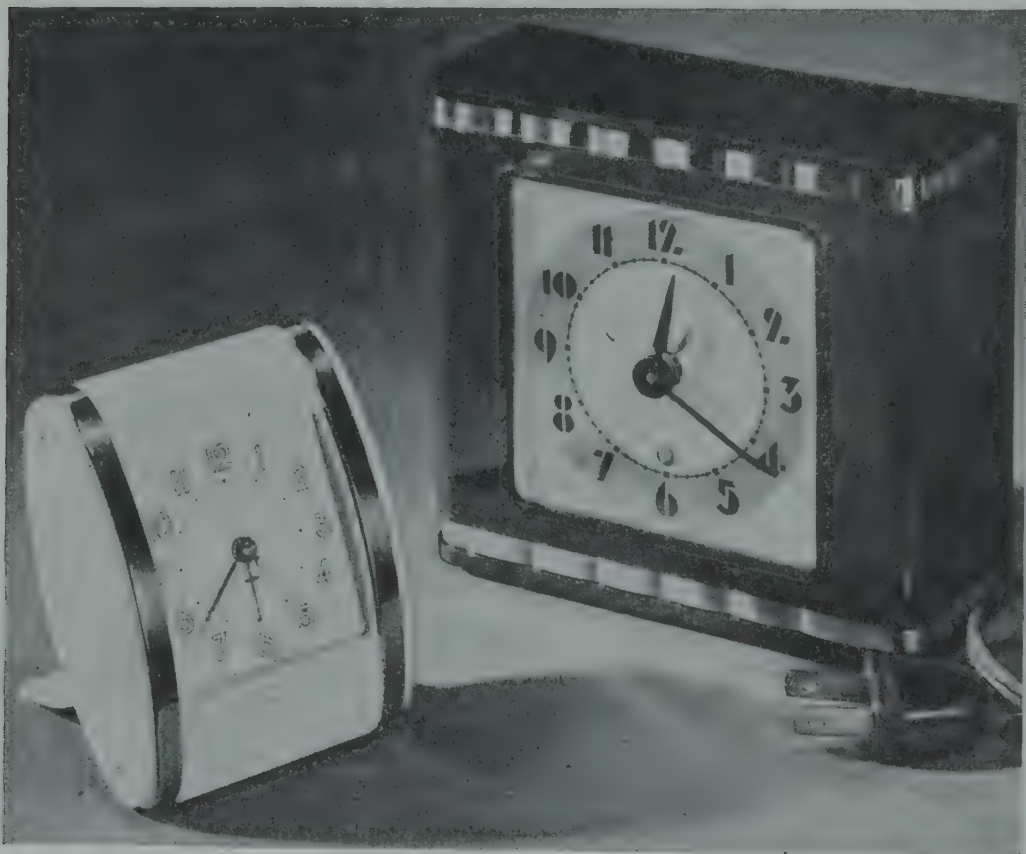


FIG. 11.3. The ivory traveling clock is molded from "Beetle" and the blue desk clock is molded from "Plaskon." (Courtesy of American Cyanamid Company, Plastics Division.)

The many methods of fabrication are of course a desirable characteristic in the extension of ureas into many diversified fields. Molding, laminating, coatings and, in rare cases, casting illustrate the workability and adaptability of this class. When such factors are combined with particularly good electrical properties, the introduction of urea-resins into electrical applications is readily under-

stood. Good dielectric strength and electrical arc resistance have caused the selection of ureas in preference to phenolics in many cases.

In addition to the desirable properties of urea-formaldehyde resins discussed above, they also exhibit the general properties characteristic of many resins. For example, they are odorless, tasteless, light in weight, rigid, thermosetting, and capable of producing hard surfaces.

The marketing of urea resins in many diverse forms such as molding powders, resin solutions, laminating varnishes, and adhesive cements is indicative of the variability of their ultimate uses. The combination of properties discussed is responsible for its popularity in such applications as laminated table tops, fountain bar tops, refrigerator parts, wall paneling, adhesive glues, advertising units, machine housings and bases, tableware, clock cases (Figure 11.3), light shades, textile finishes, and electrical units.

An interesting laminated structure possessing the typical colorability feature of ureas may be produced by using urea-resin sheeting as the top layer and a less expensive (phenolic) resin as the principal binder. In this way, low cost and required beauty may be obtained. The electrical properties are utilized in the manufacture of electrical control switches. The transparent, glass-like effect is indispensable in the production of urea-resin impregnated paper and wood veneer. In both cases the original true color is desired in the final product and a transparent impregnating material is required.

Some trade names used for urea-formaldehyde resins are: Bakelite Urea, Beetle, and Plaskon.

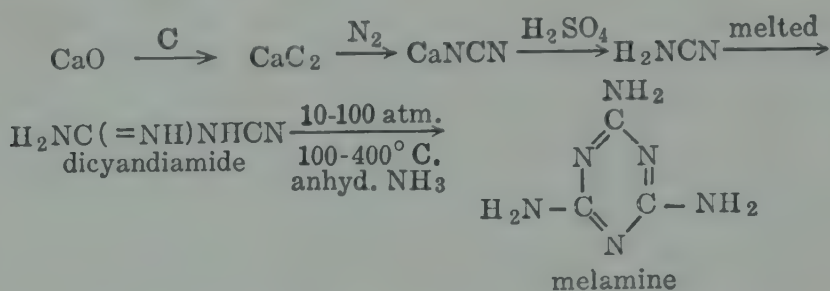
MELAMINE RESINS

The resins derived from the use of melamine in place of urea in combinations with formaldehyde are so comparable to the urea derivatives that they may be included in this family. The first step in the reactions by which these two resins are produced is, in both cases, the reaction of formaldehyde with the amino group. The same type of reaction is also involved in the preparation of aniline-formaldehyde resins, which will be mentioned later.

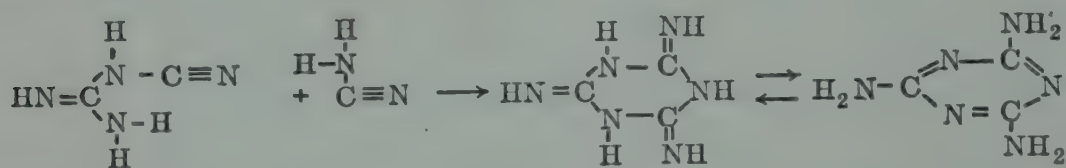
Melamine resins were first made available in appreciable quantities in 1939. It is interesting to note that even as recently as 1938, melamine sold for approximately \$40 a pound.² The price in 1944 was 40 cents a pound when purchased in large quantities. The basic raw materials used in the preparation of melamine are limestone

² McClellan, *Ind. Eng. Chem.* 32, 1181 (1940).

and coke. The following scheme shows the preparation of melamine from limestone and coke:



The exact mechanism of the reaction by which melamine is obtained from dicyandiamide is not known. It is possible that some of the dicyandiamide dissociates to form cyanamide. A molecule of cyanamide is capable of reacting with a molecule of dicyandiamide to form melamine.



Melamine is capable of reacting with from one to six moles of formaldehyde. Of these six possible compounds, only the trimethylolmelamine and the hexamethylolmelamine have been isolated. These compounds may polymerize by self-condensation or by condensation with unchanged molecules of melamine to form complex polymers similar to those formed from methylolureas.

In the case of the melamine resins a wide latitude of curing conditions has resulted in the introduction of many new products. Alkaline fillers or other resinous types such as polyvinyl acetals which will form cross-linkages in the presence of an alkaline catalyst can be mixed with the melamines for fabrication. Properties such as heat resistance, which are not generally characteristic of the ureas may, in this way, be incorporated.

Generally, however, the properties exhibited by the melamine resins are those which are typical of the urea-formaldehyde resins. Colorability, translucency, abrasion resistance and dielectric strength are associated with both classes of resins. With respect to other properties such as surface hardness, general chemical resistance, arc resistance, and dimensional stability in contact with boiling water, the melamine resins are proving superior to the urea resins.

These combinations of valuable properties are responsible for the rapid rise in the popularity of melamine resins. The colorability and

hot-water resistance are fundamental necessities in the preparation of tableware, novelties, buttons (see Figure 11.4) and toilet articles. Excellent arc resistance, high dielectric strength maintained over a wide range of temperatures, and compatibility with a variety of fillers are factors which have caused the adaptation of melamine resins to such purposes as ignition system parts, electrical units, circuit breakers, and switch plates. Such products as table tops,



FIG. 11.4. Buttons made from melamine-formaldehyde polymer. (Courtesy of American Cyanamid Company, Plastics Division.)

fountain bar-tops, plywood and laminated products can be conveniently fabricated from melamine resins because of their excellent adhesive quality, chemical resistance, abrasion resistance, hardness, and colorability. An interesting application is the incorporation of trimethylolmelamine in paper in the beater stage, followed by subsequent drying and polymerization of the trimethylolmelamine. This resin-treated paper has markedly increased wet and dry strength. Its wet strength is such that it can be immersed in water for hours

without losing its strength. Such a paper is obviously of great value for wrapping purposes.

Melamine-formaldehyde and urea-formaldehyde resins have also found wide application in the treatment of fabrics to produce crease-proof and shrink-proof characteristics. By incorporating a definite percentage of resin into the fiber, the flexibility and appearance can be maintained with introduction of these valuable characteristics. The percentage of resin used varies with the nature of the fabric used, e.g., wool requires approximately 5% of resin, cotton or linen, 12%, and rayon, 18%. The treated fabric is produced by passing it through an impregnating bath where heavy rollers actually force the water solution of the acid-catalyzed resin into the fibers. After drying and curing for 5–7 minutes at 280° F., or for 2–3 minutes at 310° F., the finished fabric is obtained.

The application of melamine resins to the field of coatings is comparable to the use of ureas. Preparation of the resins in alcoholic solution in order to produce a type soluble in organic solvents, modification by addition of alkyd resins, and chemical plasticization with phthalates or castor oil are useful operations in coating formulations. The particular advantages of the melamine-alkyd combinations over those of the urea-alkyd composition are:

- (a) Increased hardness
- (b) Heat stability at varying baking temperatures
- (c) Improved chemical resistance.

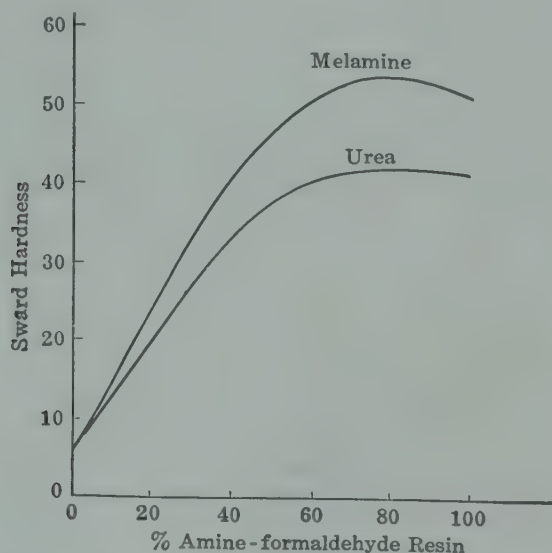


FIG. 11.5. Comparative hardness of amine-formaldehyde coatings. (Hodgkins, Hovey, Hewett, Barret and Meeske, *Ind. Eng. Chem.* **33**, 775, 1941.)

The first of these is illustrated in Figure 11.5. These results were obtained when mixtures of amine-formaldehyde resins and a semi-drying alkyd resin were baked for one-half hour at 250° F. Figure 11.6 illustrates the decrease in hardness of a urea-alkyd resin mixture caused by excessive heating, and the stability of the melamine-formaldehyde resin under the same conditions.

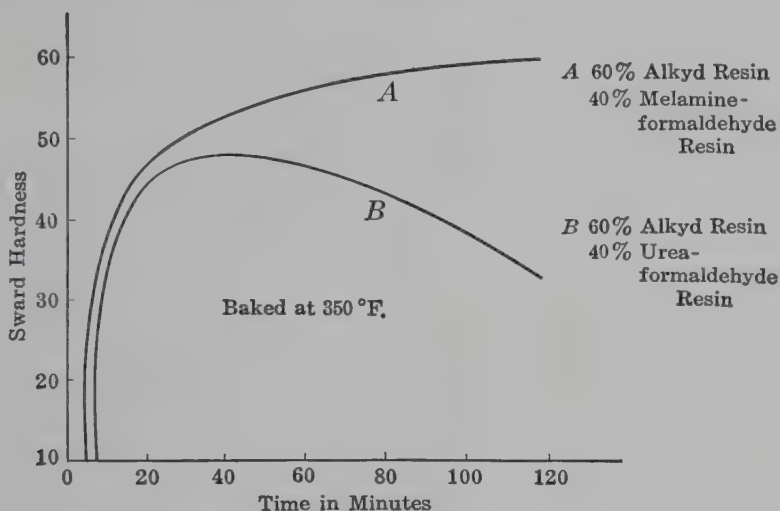


FIG. 11.6. Effect of baking time upon hardness of amine-formaldehyde coatings. (Hodgkins, Hovey, Hewett, Barret and Meeske, *Ind. Eng. Chem.* 33, 775, 1941.)

Sold in the form of solid resins, adhesive solutions and granular or powdered molding compounds containing any desirable filler, the product is identified by the following trade names: Melmac, Catalin Melamine, or Plaskon Melamine.

REMAINING TYPES

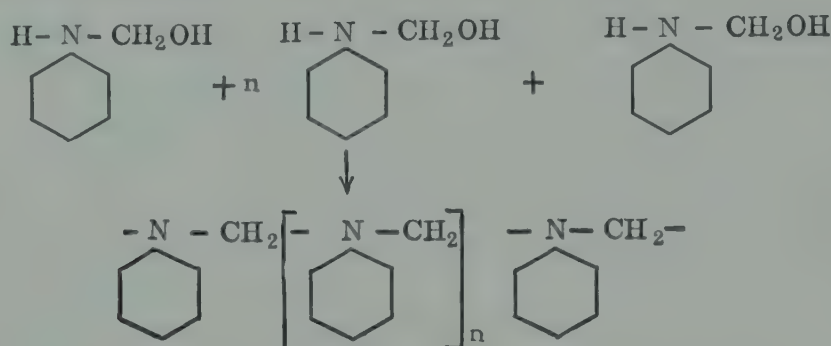
Thiourea Resins: These resins may be produced from thiourea H_2NCNH_2 and formaldehyde in the same manner as those produced



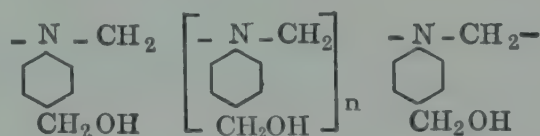
from urea and formaldehyde. Although known for some time, these resins have never reached major industrial importance because of their injurious staining effect on steel molds. The higher water resistance of these products as compared to that obtained with urea-formaldehyde resins is the principal reason why they are used in a few instances.

Aniline-Formaldehyde Resins: This class of resinous products is typical of those products which may be formed from the general

reaction of aromatic amines with formaldehyde or other aldehydes, either aliphatic or aromatic. When one mole of aniline and one mole of formaldehyde are allowed to react, a soluble, fusible (thermoplastic) product is formed. These properties indicate that the resin is a linear polymer with no cross-linkages. The reaction may be formulated as follows:



If an excess of formaldehyde is used, the solubility and fusibility decrease. This may be due to the introduction of cross-linkages. It is well-known that phenol and amine groups increase the reactivity of hydrogen atoms in the ortho and para positions of the benzene ring. The linear polymers first formed may react with formaldehyde to form reactive methylol groups, e.g.,



These methylol groups could then react with other chains to form complex branched or cross-linked polymers.

Since most aniline-formaldehyde resins are made from equimolecular amounts of aniline and formaldehyde, they exhibit typical thermoplastic properties. Fabrication methods must be those used for thermoplastic resins. Molding, for example, consists of softening, shaping, and then hardening by cooling before removal from the mold.

This class of resin is becoming increasingly popular as an insulating medium in high frequency electrical fields. Often used to replace mica, ceramics, phenolics or polystyrene, the aniline-formaldehyde resins are proving of value because of their low power factor, high dielectric strength, mechanical strength, inertness to moisture, and ease of machining.

The product is marketed industrially under the trade names Cibanite and Dilectene.

Review Questions

1. Discuss the importance of each of the following in the preparation of a urea-formaldehyde resin:

- (a) pH of catalyst
- (b) ratio of reactants
- (c) temperature.

2. Show by chemical reactions the formation of a resin from:

- (a) urea and formaldehyde
- (b) melamine and formaldehyde.

3. For what purpose may each of the following be used with a urea-formaldehyde resin:

- (a) alpha cellulose
- (b) benzoyl mercaptobenzothiazole
- (c) acetic acid
- (d) wood flour
- (e) urea
- (f) retardants?

4. Why is the use of urea-formaldehyde resins in casting limited?

5. Compare the properties of urea resins and phenolics.

6. What molding difficulties are encountered with urea resins?

7. Describe the reactions involved in the preparation of alcohol-modified urea-formaldehyde resins. What advantages do these resins have when compared with urea-formaldehyde resins?

8. How is melamine produced? Write equations for the reactions involved.

9. What advantages do the melamine-formaldehyde resins have over the urea-formaldehyde resins?

10. What methods are available for the stabilizing of urea-formaldehyde resins which are to be used in bonding applications?

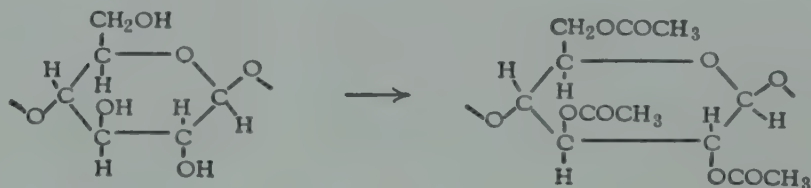
CHAPTER XII

THERMOPLASTICS

SYNTHETIC PLASTICS III: CELLULOSE DERIVATIVES

One of the most important commercial families of plastic products is composed of products derived from the basic natural material, cellulose. The plastics members of this class are worthy of the closest scrutiny not only because of the fundamental part they have played in the development of new plastics articles, but also because of their historical relationship to the introduction and perfection of many fabrication methods.

The cellulose molecule has previously been described as a polymeric chain consisting of repeated glucose units. Each of these monomeric units contains three hydroxyl groups and the existence of such reactive positions may be proved by typical acetylation methods. Thus, when cellulose is completely acetylated, cellulose triacetate is formed:

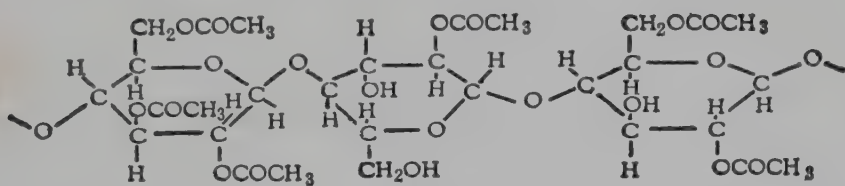


Partial hydrolysis of cellulose triacetate under carefully controlled conditions yields products which are suitable for use as plastics.

Two basic types of derivatives may be formed according to the method of treatment applied to the cellulosic raw material. Cellulose esters such as the acetate, propionate, butyrate and nitrate are formed in an acidic medium. On the other hand, by treating cellulose with alkali in order to make a sodium cellulosate and then adding an alkyl halide (Williamson synthesis) or an alkyl sulfate, cellulose ethers are formed. Such plastic materials as cellulose esters and ethers are conveniently classified as *synthetic* because chemical modification is necessary in their manufacture. To these two fundamental groups, we may add *regenerated cellulose*. Although the cellulose molecule is reproduced in a more or less degraded condition after processing manipulation, chemical reactions actually occur in

the plasticization (solution) and deplasticization (coagulation) involved in the formation of rayon or cellophane.

The preparation of the cellulose derivatives differs in many chemical features from the production of most synthetic high polymers. First, it should be emphasized that no polymerization is involved in the manufacture of these products. The polymerization has been completed in nature and the synthetic process consists merely of forming derivatives of the reactive hydroxyl groups in the cellulose molecule. Actually, as will be pointed out later, some depolymerization of the cellulose molecule occurs. Secondly, because 100% replacement of the hydroxyl groups does not result from the chemical modification, the properties exhibited will depend upon the relative proportion of hydroxyl and replaced hydroxyl groups. This latter feature also leads to the inevitable conclusion that the repeating units of the cellulose esters or ethers need not exactly duplicate one another. The following formula, for example, might represent a portion of a cellulose acetate polymer:



The composition is described according to the average number of hydroxyl groups replaced along the chain length.

As a means of summary, the factors which are of importance in a description of the chemical structure of a cellulose derivative may be listed, together with a brief discussion of the properties which are dependent upon these factors.

1. *Type of Derivative Involved*: Obviously, this depends upon the nature of the substituent group.

2. *Degree of Degradation*: As described on p. 155, this refers to the amount of molecular weight reduction caused by the chemical process. The cellulose chain is easily cleaved into oxy- or hydroxy-cellulosic bodies. The molecular weight of the product which is ultimately formed depends upon the extent to which the breakdown reaction has proceeded. Fundamental characteristics such as viscosity in solution, tensile strength, softening point, and chemical resistance are, in turn, directly dependent upon molecular weight.

3. *Degree of Reaction*: Regardless of what derivative is involved, the properties of the product are determined in part by the relative number of hydroxyl groups which have been replaced. The factor,

degree of reaction, may refer to either the original substitution reaction or to a hydrolytic reaction carried out for regulation of the hydroxyl content. Both reactions affect the chemical composition and the properties of the product.

4. *Ratio of Mixed Substitution:* When two or more substituting groups are involved in the reaction, the properties vary according to the relative amounts of each group present. In the preparation of cellulose acetate-butyrate, for example, the ratio of acetate groups to butyrate groups is a fundamental factor in the determination of the physical and chemical properties of the mixed ester produced.

CELLULOSE NITRATE

This plastic derivative of cellulose was applied in 1869 by John Hyatt as the first practical demonstration of the value of plastics. At that time, cellulose nitrate, compounded with camphor as a plasticizer, was employed as a substitute for ivory. Gradually, new uses were discovered as the industry started its growth. The amazing features of its history are, first, that camphor still remains as one of the best plasticizers in cellulose nitrate fabrication, and, second, the plastic itself retains its popularity and sales volume. This latter fact is quite remarkable in view of the many new, diversified products which have since appeared. The greatest drawback to even greater expansion in the use of this product, of course, is its flammability. This objection is being partly overcome by choice of the proper compounding ingredients.

Manufacture.—The cotton linters used for the manufacture of the plastic base are first purified in order to remove natural oils, resinous matter and mechanically suspended impurities. The purification process usually consists of decomposing the oils and resinous matter by heating with dilute alkali, followed by thorough washing. The cotton is then bleached with alkaline hypochlorite solution, washed with water, then with dilute acid solution and finally again with water. After thorough shredding, the fibrous mass is then ready for nitration, using a mixture of nitric and sulfuric acids. The extent of substitution of the hydroxyl groups depends upon careful control of such variables as concentrations and ratio of the two acids, temperature, pressure and length of time for the reaction. Complete absence of impurities is also necessary. If complete reaction takes place, a product having a nitrogen content of 14.14% is formed. This derivative, however, is exceedingly explosive and is marketed as gun cotton.

When the substitution is carefully regulated the nitrogen content may be maintained within suitable limits and the desired properties of solubility, strength, and non-explosiveness necessary for a desirable type of plastic may be obtained. The degree of degradation which occurs during the nitration is also an important factor in determining the molecular size of the product and the ultimate properties of the plastic. Table I-12 gives the range of nitrogen content possible and the approximate chain lengths obtained in different products. Particular emphasis should be placed on the low molecular weights found in cellulose nitrate suitable for use in lacquers. The low molecular weight products, which are so desirable for the formulation of satisfactory coatings, are the result of high temperatures and pressures during the nitration reaction.

TABLE I-12. CHARACTERISTICS OF CELLULOSE NITRATE RELATING DEGREE OF SUBSTITUTION TO ULTIMATE USE ^a

Product	Nitrogen ¹ Content, Per Cent	Length of Macromolecule; No. Glucose Units
Explosives	12.1-13.8	3000-3500
Lacquers	11.5-12.1	175
Plastics	10.5-11.5	500-600

^a Del Monte, *Plastics in Engineering*, p. 71, Penton Publishing Company, Cleveland, 1942.

¹ Cellulose trinitrate — 14.14% N
 Cellulose dinitrate — 11.11% N
 Cellulose mononitrate — 6.76% N.

When the substitution has proceeded to the desired extent (replacement of approximately two hydroxyl groups per glucose unit), the product is separated from the acidic impurities by complete washing, beating, wringing and blending operations. Partial removal of water by centrifuging and "wetting" of the product with alcohol to aid in the processing is then carried out before compounding. The alcohol-wet product may then be compounded with plasticizers such as camphor or tricresyl phosphate and dyes or pigments until the desired formulation is obtained. The latter stages of compounding may be carried out by kneading either in a rotating-arm mixer or on a rubber-mill until complete incorporation of plasticizer and pigment and partial evaporation of the solvent result. The plastic is then removed and sheets or slabs approximately one inch thick are formed. Several of these slabs may then be molded firmly

together under heat and pressure, to form a single solid block. Sheets of any desired thickness, down to 0.003 inch, rods and blocks, may be cut from this large cake. When the plastic is to be used in solvent applications such as coatings or adhesives, the centrifuged product is used and is marketed as an alcohol-wet (containing 15–35% of alcohol) fluffy solid.

Fabrication.—The fabrication of cellulose nitrate products must be regulated in order to minimize the dangers resulting from its high inflammability. In most cases, the product is provided to final fabricators in the form of sheets, rods, tubes or coiled ribbons modified to satisfy any specific requirements of softening point, color, odor, hardness, or strength. Such pre-fabrication forms are produced from the processing of the plastic compounded mass which results from the kneading operation. By pressing this soft composition into blocks which may be sliced to any thickness or by extruding it in the form of rods, tubes or ribbons, stock shapes and designs result. Such products, however, are still wet with alcohol and final hardening is achieved by “seasoning” or, in other words, slow evaporation of the solvent from the prepared form.

If such a pre-fabricated stock material is used for the final fabrication, the thermoplastic nature of the plastic base is utilized in the processing. By suitable drilling, blowing, cementing, cutting, drilling, taping, polishing, extruding, swaging, or engraving operations the final form may be produced. In the molding of cellulose nitrate, for example, the granular material is not used because this form of cellulose nitrate does not weld together. Instead, solid pellets or blocks of the proper size are loaded into a hot mold and reshaped under a pressure of about 3000 lbs. per sq. in. If desired, the plastic materials may be preheated and forced into any desired shape under pressure. Almost any design or irregular shape may result from drawing or pressing simple sheets while hot and then cooling the shaped form before removal from the die. Hollow shapes, toys, balls, and Christmas tree ornaments may be formed by blowing compressed air into a capped tube or between flat sheets in a molded form, as illustrated in Figure 12.1. Fabrication methods may involve the use of “elastic memory” of the plastic. In making heel covers or decorative film coverings, for example, a properly shaped sheet stock may be stretched, while hot, to a size which is sufficiently oversize to enable it to be slipped onto the object to be covered. Then, while in the stretched, warm condition it may be “set” by plunging it into cool water. It is then placed around the object. When the sheet is reheated with the object inside, the plastic coating

shrinks toward its original dimensions and permanently grips around the product being covered.

Simpler operations such as those applied in manufacturing fountain pen barrels, buttons, toilet articles, novelty jewelry, and card cases consist merely of machining by cutting and polishing methods. In this case, the only danger which must be guarded against is overheating. Since the product is thermoplastic, the friction of machining may cause excessive softening.

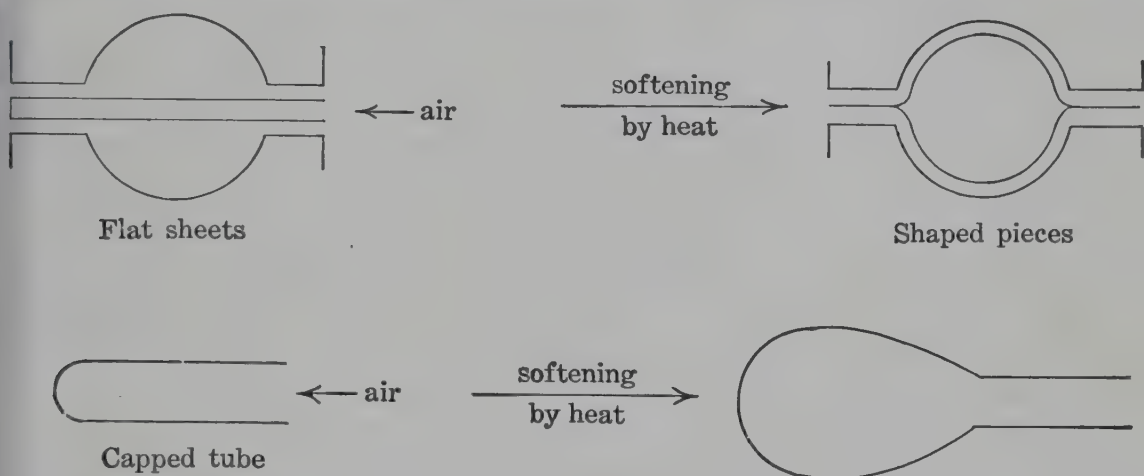


FIG. 12.1. Shaping by blowing.

Coatings.—One of the broadest applications of cellulose nitrate is its use in surface finishes and textile or paper impregnants. Quick-drying lacquers may be formulated from pyroxylin plastics modified with various plasticizers such as camphor, poly-esters or natural resins, and dissolved in suitable solvents or mixtures of solvents.

A well-known solution of cellulose nitrate and camphor in a mixture of alcohol and ether is marketed as collodion. Collodion is much too viscous a solution to be applied by either spraying or brushing. Hence, one of the first difficulties that had to be solved was the problem of dissolving the cellulose nitrate in a suitable liquid, so that the solution would not be too viscous, and at the same time dissolving enough cellulose nitrate so that after evaporation of the solvent, there would be a sufficiently thick coating of solid cellulose nitrate and plasticizer. These results may be achieved at low cost by first dissolving the cellulose nitrate in a suitable solvent and then adding a non-solvent as a diluent in order to decrease the viscosity of the solution. The most common diluents are the aliphatic and aromatic hydrocarbons. Obviously, if too much of the non-solvent diluent is added, cellulose nitrate will be precipitated. Solu-

tions of different solvents containing the same concentration of cellulose nitrate were found to have different tolerances with respect to the amount of diluent which could be added before causing precipitation. In order to compare the dilution tolerance of various solvents, the *dilution ratio* was proposed as the volume of diluent which must be added to a unit volume of standard (usually 10%) solution of cellulose nitrate to cause precipitation.

$$\text{Dilution ratio} = \frac{\text{Volume of diluent added}}{\text{Volume of original solution}}.$$

Dilution ratios vary, not only with the solvent used, but also with the nature of the diluent.

One of the most interesting facts which has been found from a study of dilution ratios is that alcohols, which possess no solvent power² for cellulose nitrate, can exert a solvent action when mixed with good solvents for cellulose nitrate. For example, a solution of cellulose nitrate in *n*-butyl acetate was found to have a dilution ratio of 2.93 when toluene was used as the diluent. When a 50-50 mixture of *n*-butyl acetate and *n*-butyl alcohol was used as the solvent, the dilution ratio was 3.45. In this case the replacement of half of the *n*-butyl acetate (a good solvent) with *n*-butyl alcohol (a non-solvent) actually increased the solvent power of the solution. Such a mixed solvent is sometimes called a "fortified solvent." It should not be inferred that the substitution of butyl alcohol (or other alcohols) will always increase the dilution ratio. In some cases the dilution ratio is the same as that of the pure solvent and in other cases it is appreciably less than that of the pure solvent.

The method of applying the lacquer—dipping, spraying or brushing,—is an important factor in determining the nature of the solvents and diluents to be used. In the formulation of dipping lacquers, most of the solvent consists of low-boiling liquids. About 10-15% of high-boiling solvents and a smaller percentage of medium-boiling solvents are also used. The diluent should be selected from the more volatile diluents. Since a large proportion of the liquid is quite volatile, the lacquer sets quickly, so that very little of the solution will drain off. The high-boiling solvents are necessary to provide sufficient flow of the lacquer to form a coating of uniform thickness. They also promote the formation of a high gloss on the surface.

² Methanol dissolves cellulose nitrate suitable for use as collodion; ethyl alcohol dissolves only cellulose nitrate of lower nitrogen content. Neither ethyl alcohol nor any higher alcohols are solvents for cellulose nitrate used in lacquers.

One of the most important factors involved in making a spraying lacquer is the evaporation which takes place when tiny droplets of the solution are sprayed from the atomizer onto the surface to be coated. In order to prevent too rapid evaporation, medium-boiling solvents are used to the extent of 60–80% of the total solvent. Volatile solvents (10–25%), high-boiling solvents (5–10%) and medium-boiling diluents are also used.

For brushing lacquers, high-boiling, slow evaporating solvents and diluents are used principally, together with small proportions of medium and low-boiling solvents.

In deciding upon the proper solvents for use in a lacquer or an adhesive, it is highly desirable that the mixture of solvents should exert approximately equal solvent power on all of the ingredients, the basic plastic, the plasticizer and any added resin.

The hardness of the coating will depend upon the nature and amount of plasticizer used. Small amounts of plasticizer will cause the formation of a harder surface than is obtained when larger amounts of plasticizers are used. Natural resins also may be added to the coatings to increase the hardness.

Properties and Applications.—Many of the characteristics responsible for the popularity of nitrocellulose plastics have already been pointed out. The extreme ease of workability and the variety of fabrication methods possible permit a widespread choice of design. Added to this—and of particular importance in coating applications—is the property of excellent colorability in the nitrocellulose plastics. The plastic product itself is available in transparent, translucent and opaque effects, and any desired color may be incorporated. Familiar to even the layman, also, are the excellent toughness and mechanical strength of the fabricated products. The incorporation of suitable plasticizers causes a marked improvement in such properties as impact resistance and resiliency. Worthy of mention, also, is the excellent chemical resistance of films produced from nitrocellulose. They possess the ability to withstand, without apparent effect, such diversified agents as animal and vegetable oils, dilute acids, alkalies and water. The water absorption is sufficiently low (0.6–2.0% for 24-hr. immersion) to permit use of this plastic in tableware, toilet articles, and packaging foils. Very poor resistance to oxygenated solvents such as alcohols, ketones, and esters is exhibited because of the solubility of the plastic in these solvent classes.

Included in the disadvantages of this plastic type are its flammability and decomposition on continued exposure to light. The flammability of cellulose nitrate is well known. Although not of the

same explosive nature as those cellulose derivatives containing a higher percentage of nitrogen, the rate of burning of cellulose nitrate plastics is very high. Care must constantly be exercised in the production and use of such products to prevent ignition. This undesirable characteristic has been improved to some extent in recent years by the use of flame-resistant phosphate plasticizers. The poor resistance of cellulose nitrate to light is particularly objectionable in clear films. Discoloration and embrittlement accompany the changes caused by exposure to the direct rays of the sun. The greatest objection to this property was that which arose as a result of cellulose nitrate being used as laminating film in safety glass. Originally clear and colorless, the film became yellowish-brown after exposure to sunlight. In common with other thermoplastics, cellulose nitrate plastic loses its shape at elevated temperatures. It is not used at temperatures above 60° C., for it softens in the region of 70° C.

The uses of cellulose nitrate are so diversified that even a representative list of its applications becomes involved. Decorative finishes, printed textiles, artificial leather, drafting instruments, heel covers, fountain pen barrels, piano keys, packaging foils, photographic film, tool handles and novelties are some of the products which are easily fabricated and machined from the basic plastic. The trade names include Amerith, Nitron, Nixonoid, Pyralin, Celluloid, and Hercules Cellulose Nitrate flakes.

CELLULOSE ACETATE

Manufacture.—The most widely used cellulose derivative—cellulose acetate—is manufactured by the same method as cellulose nitrate, with only slight variations. The purified and macerated cotton linters are first activated by treatment with glacial acetic acid and a catalyst such as zinc chloride, phosphoric acid, sulfuric acid or chloroacetic acid. Then, the actual acetylation reaction occurs after the addition of acetic anhydride and, usually, a liquid such as methylene chloride or acetic acid which serves as a solvent for the product, cellulose triacetate. As the temperature of reaction is carefully controlled and the hydroxyl groups are gradually replaced, the cellulosic base is gradually converted into a thick syrup with the acid and solvent mixture. This reaction leads to the formation of a completely substituted derivative, namely cellulose triacetate. However, cellulose triacetate is insoluble in most of the common organic solvents and is not suitable for any commercial use. Very desirable forms of

cellulose acetate can be obtained by partial hydrolysis of the triacetate. This is accomplished by diluting the reaction mixture with water and maintaining it at a definite temperature for a stated period of time. Much more satisfactory products are obtained by this procedure of acetylating completely and then partially hydrolyzing the triacetate, than by attempting to control partial acetylation. The precipitation and purification of the plastic derivative from this point is simply a series of physical operations. Filtration, washing, and drying to the desired moisture content prepares the plastic for compounding into a molding powder or for eventual use in coating or adhesive formulations.

At this stage, the properties which will be exhibited by the acetate derivative are dependent upon the molecular weight of the polymeric chains and the chemical constitution of these chains. The molecular weight is determined by the extent of degradation which occurred during the acetylation.

The chemical constitution depends upon the degree of acetylation or more properly the degree of hydrolysis of the triacetyl derivative. The dependence of the application methods upon the composition, for example, is illustrated in Table II-12.

TABLE II-12. CHARACTERISTICS OF CELLULOSE ACETATE ^a
(As dependent on degree of substitution)

Substance	Acetyl Groups as Per Cent of Molecular Weight
Cellulose triacetate	44.8
Cellulose diacetate	35.0
Plastics	36.5-38.5
Textile grades	38.0-39.4
Lacquers	37.5-39.5

^a Del Monte, *Plastics in Engineering*, p. 73, Penton Publishing Company, Cleveland, 1942.

Compounding and Fabrication.—The cellulose acetate base may be produced in the form of standard pre-fabricated sheets, rods or tubes as in the case of cellulose nitrate. If these are to be prepared, volatile solvents may be mixed with the material during compounding with plasticizer, dyes, and other modifying agents. Final shaping and pressing of the solvenized dough must then be followed by "seasoning" (Figure 12.2) in order to remove the solvent and complete the final hardening of the product. The fabrication of these standard

shapes into the final products consists merely of the same physical operations that are employed with cellulose nitrate. By cutting, punching, cementing, sawing, drilling, etc., the finished product can be obtained.



FIG. 12.2. Lumarith (cellulose acetate) sheets hung in heated vaults for seasoning. (Courtesy of Celanese Celluloid Corporation.)

The most popular method of applying cellulose acetate is by a molding procedure involving the use of a powdered or granular molding powder in either a compression or injection molding machine. The acetate differs from the nitrate in the fact that powdered cellulose acetate is capable of flowing into a compact mass of excellent mechanical strength. Secondly, injection molding which is impractical in the case of cellulose nitrate may be conveniently and economically applied to cellulose acetate.

The production of molding powders from the basic cellulose acetate depends upon the incorporation of modifying agents. The mixing operation may be carried out in any hot mixing equipment. A rubber mill or internal mixer of the Banbury type is usually employed to homogenize the ingredients. Then, the uniform mass must be ground, various batches blended and packed for shipment. If a cold mixing operation is preferred, the molding powder may be formed in much the same way as that employed for the formation of sheets and tubes. The compounding may be carried out in the presence of a volatile solvent and, after the ingredients are thoroughly incorporated into the dough-like, solvenized plastic, the product may be dried to the proper point for molding.

The most important compounding agent in the formation of acetate molding powders is the plasticizer. Most thermoplastics depend upon the proper choice of plasticizer to attain the highest possible degree of strength, resiliency and workability. Cellulose acetate is no exception. First, the plasticizing agent must be chosen with the aim of obtaining the most beneficial results of processing. Various degrees of flow or softness can be produced by varying the nature and the amount of plasticizing agent. Esters such as diethyl phthalate, dibutyl phthalate, dibutyl tartrate, diphenyl phthalate, tricresyl phosphate, alkyl glycolates and citrates or miscellaneous types such as camphor and substituted sulfonamides are among the plasticizers which have been used successfully with cellulose acetate.

TABLE III-12. COMPARISON OF PROPERTIES OF CELLULOSE ACETATE MOLDING COMPOSITIONS CONTAINING DIFFERENT PLASTICIZERS ^a
66% Hercules Cellulose Acetate (PM Grade) and 34% Plasticizer

Plasticizer	Hardness (Rockwell)	Flexural Strength, lbs./sq. in.	Per Cent Water Absorbed 48 Hours (room temp.)
Dimethyl phthalate	32	5840	1.14
Diethyl phthalate	15	5680	1.20
Di-(methylcellosolve)-phthalate	31	5370	1.48
Methyl phthalyl ethyl glycollate	65	7110	0.77
Ethyl phthalyl ethyl glycollate	50	6930	0.97
Ethyl <i>p</i> -toluene ethyl sulfonamide	90	9160	0.85
Diethylene glycol dipropionate	-45	4500	1.48

^a Data taken from *Hercules Cellulose Acetate*, p. 23, Hercules Powder Company, Wilmington, 1941.

Furthermore, the amount of plasticizer which can be used varies over very wide limits, from 10% to 70%. Thus it is easily seen that the possibilities of variation of plasticization of cellulose acetate are almost limitless. Variations in hardness, flexural strength and water absorption of cellulose acetate compounded with different plasticizers are shown in Table III-12.

The following is a typical list of commercially available molding powders³ which vary with respect to the nature and the amount of plasticizer used:

Grade VH—very hard—used for making mottled objects.

Grade H—hard—used for making slabs.

Grade MH—medium hard—used for making novelties and heat-resistant articles.

Grade M—medium—for general use and making novelties.

Grade MS—medium soft—has good impact resistance and is used for general injection molding.

Grade S—soft—used for making relatively thin objects; has good weldability.

Grade VS—very soft—for fine moldings requiring a long period of flow in the mold; good weldability.

The final molding and the design of the product being shaped determine to a large extent the degree of flow which must be employed. It should be remembered, however, that increasing amounts of plasticizer render the final product less resistant to heat. Often a compromise between ease of fabrication and desired properties must be effected. Secondly, the plasticizer must be selected for the production of the most desirable properties in the finished product. The inherent qualities of strength—even in the absence of fillers—associated with the thermoplastics depend upon proper plasticization. The stability and long-life of the product depend, therefore, on the permanence of the plasticizing agent. Whether the plasticizer is of a *solvent* or *non-solvent* type it must be retained in the molded product and it must contribute to the maintenance of desirable properties. Best results are frequently obtained by using two or more different plasticizers.

Cellulose acetate derivatives are much like the nitrates in that they form readily applied and quick-drying lacquers. The proper solvents, diluents and plasticizers may be chosen to produce any desired factors of drying time, gloss and hardness. The greater

³ Grades manufactured by Monsanto Chemical Co.

degree of adhesion to a variety of surfaces which is attained with cellulose nitrate makes it more valuable than the acetate in many cases. The high flammability of the former, however, has caused its replacement by the acetate, particularly in foil or film coating applications. The importance of the volatilities and dissolving properties of solvents previously discussed in connection with cellulose nitrate lacquers holds equally well for cellulose acetate lacquers.

A spraying lacquer for general purpose coatings can be made according to the following formula:⁴

Hercules LL-1 Cellulose Acetate	7.0 parts
Rezyl 14	2.1 parts
Santicizer M-17	2.1 parts
Acetone	46.8 parts
Methyl acetate	8.3 parts
Ethyl lactate	8.3 parts
1-Nitropropane	6.8 parts
Butanol	1.4 parts
When dissolved, add, while stirring,	
Methyl cellosolve acetate	3.9 parts
Toluene	13.3 parts

Cellulose acetate can be obtained in fiber form and marketed as acetate rayon. The product which is produced as yarn contains approximately 39.1% of acetyl groups, or the equivalent of a little more than two hydroxyl groups substituted per glucose unit. The process applied in the fabrication of acetate yarn is that of solution, extrusion with simultaneous evaporation, spinning, and twisting. The cellulose acetate, regulated by hydrolysis to the proper acetyl content, may be dissolved in ester or ketone (usually acetone) solvents. The viscosity and concentration may be varied to satisfy the requirements of fabrication, but the amount in solution generally varies between the limits of 18–25%. The spinning operation is carried out by extruding through fine orifices into a chamber heated by warm air. As the solvent evaporates, the solid fiber is caught and wound. The denier of the yarn is varied by changing the dimensions of the orifice or by regulation of the speed of extrusion and winding. Tension on the fiber during the spinning operation decreases the thickness.

Properties and Applications.—The most striking difference between the properties of the acetate as compared with those of the nitrate is the low burning rate of the former. Although the acetate

⁴ *Hercules Cellulose Acetate*, p. 21, Hercules Powder Co., Wilmington, 1943.

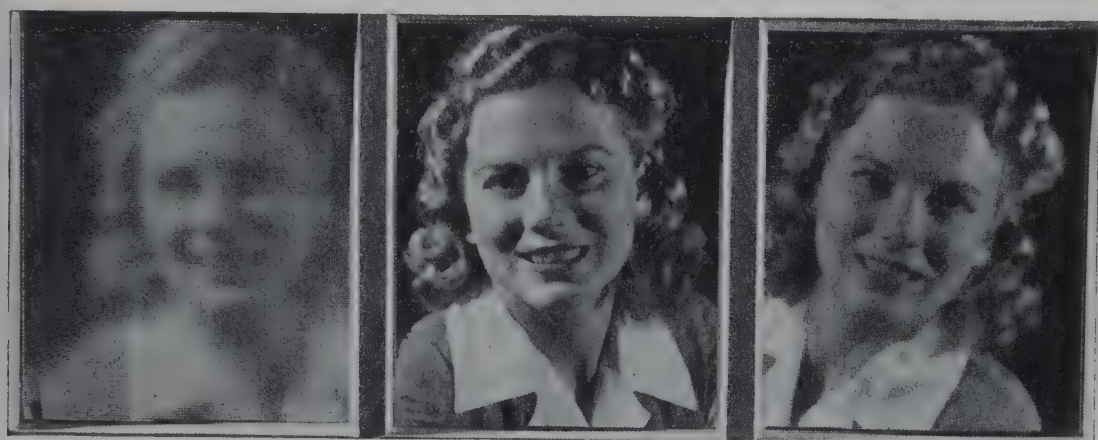
will burn, combustion is slow enough to eliminate any danger. In the final analysis, the actual rate is dependent upon the compounding agents present. Such plasticizers as biphenyl or tricresyl phosphate markedly decrease the rate of combustion. The acetates also offer a striking contrast to the nitrates in the property of moldability. General adaptability to all types of molding has been chiefly responsible for the rise of cellulose acetate to its position of supremacy in the thermoplastic class. Molders have been particularly interested in the narrow temperature range required to soften cellulose acetate and the high degree of flow in the mold which is evidenced during processing. Because of such features, complicated forms may be produced without strains or apparent weld lines in the fabricated piece.

The acetate is comparable to the nitrate with respect to the properties of colorability, machinability, and mechanical strength. The first two mentioned are of considerable importance and are necessary in applications requiring designs or complicated forms. Likewise, both esters have high impact or shock resistance, together with tensile, flexural and compressive strengths ample for most purposes. The high impact strength of cellulose acetate plastic is shown by the fact that a 12-pound iron ball can be dropped from a height of 10 feet on a $\frac{1}{8}$ -inch thick sheet of properly compounded cellulose acetate without breaking the plastic.

Cellulose acetate is a tough plastic, though less tough than ethyl cellulose. For this reason it is widely used wherever rough usage, vibration and shock are likely to be encountered. This toughness is also of value in making strong, thin-walled, display containers and oil cans. Coatings made from cellulose acetate are very durable and its toughness prevents cracking when the coated article is flexed or bent. Most cellulose acetate plastics contain from 25–40% of plasticizer or filler. Exclusive use of liquid, softening plasticizers causes a decrease in tensile strength and hardness, while elongation, impact strength and cold flow increase as the percentage of plasticizer increases. Substitution of hardening agents such as triphenyl phosphate, camphor and sucrose octa-acetate for a portion of the plasticizer causes a desirable decrease in elongation and cold flow, but the impact resistance is also decreased.

Cellulose acetate can be obtained as a transparent or an opaque sheet and can be colored almost any desired shade. Figure 12.3 is a triple exposure which illustrates the visibility of three cellulose acetate glazing materials. The first exposure is through Vimlite, a wire-reinforced cellulose acetate sheet which is used for windows in troop houses, solaria, barns and hot houses. The middle exposure was

taken through clear cellulose acetate plastic which is used wherever perfect vision is required. It is used in gliders, airplanes and in sentry boxes for anti-aircraft domes. The last picture was photographed through a combination of wire and two thicknesses of cellulose acetate sheeting. This combination is the strongest of the three and is used for partitions and windows in shell-loading plants. It is also used for pre-fabricated troop shelters because it can be shipped without breakage and with a minimum of packing.



Vimlite
(Wire and
Lumarith)

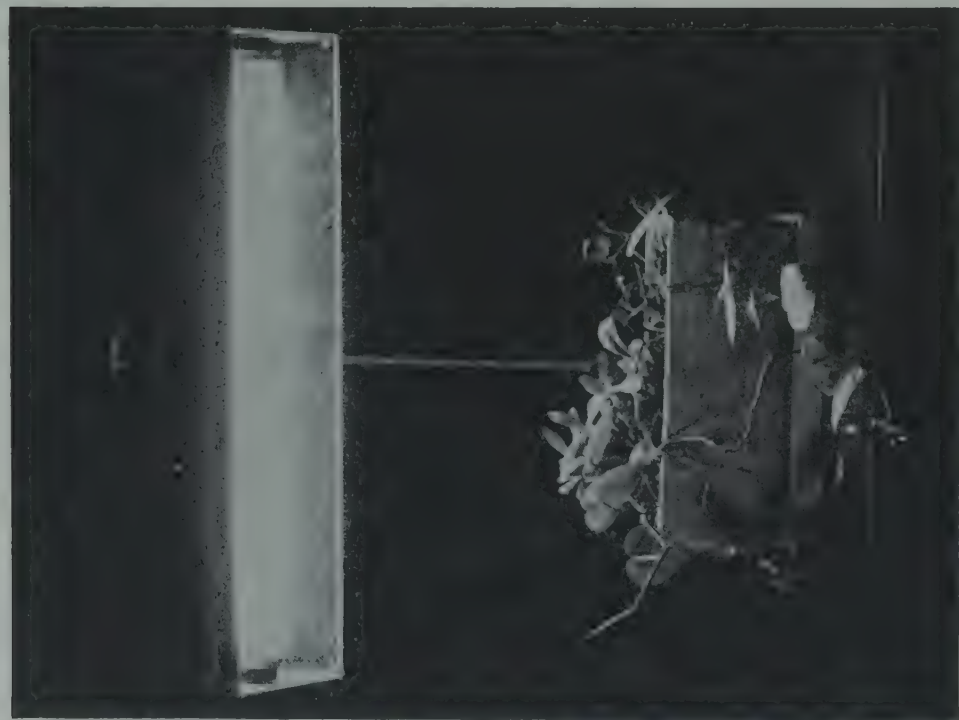
Lumarith
(Clear cellulose
acetate plastic)

Lumapane
(Wire and two
thicknesses of
Lumarith)

FIG. 12.3. (Courtesy of Celanese Celluloid Corporation.)

An interesting application of cellulose acetate sheeting is known as Louverplas. It consists of a thin sheet of the plastic composed of alternate transparent sections and opaque obstructions called louvers, running parallel to each other. The louvers may be black, white, ivory or pink. When such a sheet is placed over a fluorescent lamp, the light is directed through the transparent sections and the stray rays which normally cause glare are trapped by the louvers and re-directed. The result is shown in the two pictures in Figure 12.4.

The electrical properties of cellulose acetate are adequate for many purposes, even though these properties are not as good as the electrical properties of polystyrene and polyvinyl copolymers. Cellulose acetate exhibits high internal and surface resistance to the passage of an



4A



4B

FIG. 12.4. The lamp in Figure 4A, unshielded, produces glare. This condition is corrected by a "Louverplas" covering, as shown in Figure 4B. (Courtesy Du Pont Company.)

electric current. It is satisfactory as an insulator for wires carrying an electric current and it can be molded to form outlet plugs, light switches, and switch plates.

The chemical resistance is also generally good, but certain exceptions must be considered in its application. Like the nitrate, the acetate derivatives are resistant to many chemicals—oils, weak acids, weak alkalies, ethers—but are readily dissolved by ketones and esters and are decomposed by strong acids and strong alkalies.

The limiting or undesirable properties of the acetate may be summarized as follows:

1. *High Water Absorption:* The actual values are dependent upon the degree of degradation and acetylation involved in the preparation, but some absorption values determined by 24 hours of immersion are as high as 7%. The resistance to water is increased as the acetylation is increased, but, in such a case, moldability is sacrificed. However, a highly acetylated (41.2% acetyl) cellulose acetate has been developed which can be molded by both compression and injection methods and which absorbs only 0.95–1.2% of water after 96 hours of immersion.

2. *Heat Resistance:* Cellulose acetate plastics have rather low softening points, 60–97° C. The heat distortion points range from 50–68° C. However, the plastic does not decompose or discolor even at the high temperatures (150–260° C.) used for injection molding.

3. *Dimensional Instability:* Cellulose acetate is subject to cold flow and dimensional changes when under stress.

The acetate is applied more broadly than any other cellulose derivative. Such diversified forms as films, foils, sheets, rods, tubes, lacquers, acetate silk, molding powders and plasticized doughs are included in the merchandising of this plastic. Eventually, by final fabrications, such materials as tool handles, safety film, lighting screens, decorative moldings, radio cabinets, safety glass, weather-stripping, electrical plugs, switches, advertising displays and refrigerator parts may be formed and marketed. A pillbox for carrying medical supplies such as sulfadiazine tablets has been fabricated from a cellulose acetate molding compound having a fairly high acetyl content. This box is so tough that a man can stand on it without crushing it. A wide diversification of applications may be met by this plastic due to the combinations of relatively low cost, colorability, strength, electrical and chemical resistance. It is marketed under the trade names: Fibestos, Lumarith, Nixonite, Plastacele, Tenite I, Bakelite Cellulose Acetate.

CELLULOSE ACETATE-BUTYRATE

The manufacture and processing of the mixed cellulose acetate-butyrate ester is very similar to that described above for cellulose acetate. Naturally in the preparation, however, butyric acid or its anhydride is used in conjunction with acetic anhydride in the esterification reaction. Part of the hydroxyl groups are replaced by the butyrate radical, and the resultant properties of the plastic become dependent upon the ratio of acetate to butyrate groups combined in the polymer. In addition, the molecular weight and the extent of acylation play their parts.

After preparation of the base resin, fabrication or development of pre-fabricated forms may proceed in the usual manner as with cellulose acetate. It is interesting to note that smaller amounts of plasticizer are necessary for the plasticization of cellulose acetate-butyrate than are used with cellulose acetate. The main difference between the two plastics bases lies in the divergence among certain of their properties. The mixed ester, for example, has much better moisture



FIG. 12.5. Lightning arresters housed in transparent Tenite plastic.
(Courtesy of Tennessee Eastman Corporation.)

resistance than the acetate. The maximum water absorption approximates 2% and it may be used in contact with water without danger of bleaching. Also, improved dimensional stability results from the inclusion of butyrate groups. Parts for refrigerators and automobiles or aircraft may be built with greater assurance of permanent retention of shape. Figure 12.5 shows a lightning arrester housed in transparent cellulose acetate-butyrate plastic. Finally, the acetate-butyrate retains all of the desirable features of moldability associated with the acetate and, in addition, shows a marked improvement in its moldability around inserts.

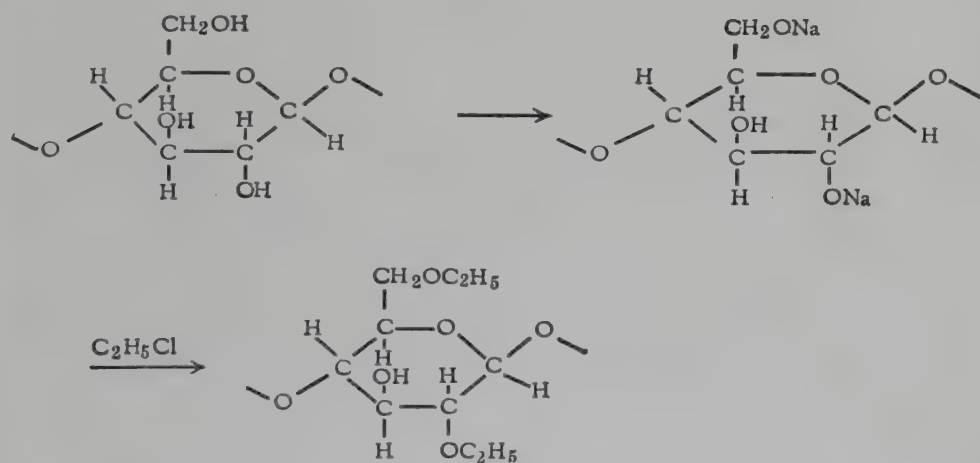
Cellulose acetate-butyrate yarn may be produced from the flake product by dry extrusion. The solid, after careful dehydration by infra-red treatment, is fed into an extruder equipped with a multiple-orifice die. Fine fibers may be extruded at high speed (.010 in. diameter at rate of 1140 ft. per minute⁵) provided the cooling arrangement is suitable.

This cellulose derivative is sold under the trade names, Tenite II, Rextrude, Hercose C.

Cellulose acetate-propionate is also available commercially and has better resistance to moisture than cellulose acetate. It is used principally in making lacquers. This mixed ester is marketed as Hercose AP.

ETHYL CELLULOSE

Manufacture.—Ethyl cellulose differs from the cellulose types previously discussed because of the fact that it is formed by an alkaline treatment of cellulose followed by alkylation. Such a series of reactions results in the formation of an *ether*. The formation of a diethyl cellulose may be indicated as follows:



As in the case of other cellulose derivatives, even if the percentage of ethoxyl present indicates the existence of diethyl cellulose, it does not mean that there are two ethoxyl groups in each glucose unit. There may be three ethoxyl groups in one glucose unit, one in another and two in still another glucose unit. The percentage simply represents the average number of substituent groups per glucose unit.

The alkaline treatment consists of subjecting the purified cotton linters or wood pulp used as the starting material to the action of an

⁵ *Plastics Catalog*, 1943 edition, p. 116, published by Plastics Catalog Corporation, New York.

18–20% sodium hydroxide solution. The treated cellulose swells as the alkali cellulose is formed. After removal of the excess alkali to such an extent that the product contains 110–125% of liquid, the ethylating reagent, ethyl chloride or diethyl sulfate, is added. An excess of the alkylating agent is always used. A temperature of 70–80° C., is used with diethyl sulfate and a temperature of about 130° C., is necessary when ethyl chloride is the ethylating agent. Slow addition of the ethylating agent will cause the introduction of a higher percentage of ethoxyl groups than will be obtained if all of the reagent is added at once. The resultant plastic product is then purified by dissolving in alcohol and precipitating with water. Filtrations and washings result in the preparation of a pure plastic base.

The percentage of ethoxyl groups present and the extent of degradation of the cellulose during the chemical reactions involved in the preparation, have an important bearing on the physical properties of the final product. The effect of the degree of ethylation on the solubility of ethyl cellulose is interesting. A product having an ethoxyl content of 27% (monoethyl cellulose contains 23.7% ethoxyl) is soluble in water, alcohol and acetic acid. As the percentage of ethoxyl increases above 27%, the water solubility of the product decreases and the solubility in organic solvents, including drying oils, increases. The general characteristics of ethyl cellulose derivatives containing different percentages of ethoxyl groups are listed in Table IV-12. The extent of degradation of the cellulose

TABLE IV-12. CHARACTERISTICS OF ETHYL CELLULOSE

Qualities	Per Cent Ethoxyl Groups ^a
Wide compatibility	48 –49.5
Wide solubility	
Low softening point	
Good water resistance	
General desirable characteristics for plastics	46.0–48.0
Toughness	
Low temperature resistance	
Low solubility	43.0–45.0
High softening point	

^a Diethylcellulose contains 41.3% ethoxyl.

Triethylcellulose contains 54.9% ethoxyl.

derivative is an important factor in determining the solubility of the derivative and the viscosity of the solution. An ethylated cellulose containing approximately 34% ethoxyl was separated into an alcohol-soluble part and an alcohol-insoluble part. Both products had the same percentage of ethoxyl groups. The soluble portion was a more degraded ethyl cellulose than the insoluble fraction. In general, the more degraded derivatives yield solutions of lower viscosity than those obtained with less degraded cellulose derivatives.

Compounding and Fabrication.—Compounding of ethyl cellulose can be accomplished by mixing the plasticizers and modifying agents either on heated rolls (100–130° C.) or in a Banbury type masticator. As in the case of cellulose acetate and other thermoplastics, the nature and the amount of the plasticizers used are of great importance in determining the ease of fabrication and the properties of the finished product. Although most of the common plasticizers are compatible with ethyl cellulose, the most widely used are dialkyl phthalates, aryl phosphates, chlorinated biphenyl, butyl stearate, glyceryl tributyrates, vegetable oils, phenyl ethers, hydrogenated methyl abietate and sulfonamides. It is interesting to note that ethyl cellulose requires smaller percentages of plasticizer than cellulose acetate.

Various fillers and resins may be added in order to modify the properties of the final product. For example, up to 30% of zinc oxide may be added in order to improve the toughness of the plastic. Ethyl cellulose is compatible with many natural resins, phenol-formaldehyde and urea-formaldehyde resins which have not reached the thermosetting stage, cellulose nitrate and waxes. It is not compatible with polystyrene, polyvinyl esters or paraffin wax. All molding compositions contain at least 1% of stearic acid in order to prevent sticking to the mold. By the addition of suitable pigments, a wide range of colors may be obtained. After compounding, the plastic is rolled out into thin sheets and then pulverized. It can be used for compression and injection molding, extrusions, coatings and adhesives. Machining and finishing operations are performed easily, with due regard to the thermoplastic nature of the material.

A typical formula ⁶ for a clear injection molding consists of

Ethyl cellulose G-100	90 parts
Dibutyl phthalate	5 parts
Triphenyl phosphate	5 parts
Stabilizer	0.5 part

⁶ Hercules Powder Company, private communication.

Ethyl cellulose is soluble in most organic solvents except aliphatic hydrocarbons. The properties of the film obtained from different solvent combinations vary widely with respect to tensile strength, flexibility and elongation. For example, films deposited from a solvent mixture of ethylene dichloride and alcohol are brittle and show poor flexibility, while films deposited from a xylene-butanol solvent mixture show excellent strength and flexibility. In general, good, tough films are obtained when non-polar solvents such as toluene and xylene are present in major amounts when the solution turns to a gel as it dries. A satisfactory and economical solvent mixture consists of 70–90% of an aromatic hydrocarbon, e.g., benzene, toluene, xylene and 30–10% of an aliphatic alcohol, e.g., methanol, ethanol or butanol.

Properties and Applications.—The most amazing characteristic of ethyl cellulose is its ability to be compounded with such a wide variety of plasticizers, gums, waxes, natural and synthetic resins and solvents. By the proper selections of these various ingredients, almost any desired combination of gloss, weatherability, hardness, flexibility and surface adhesion may be produced. The wide range of properties which may be obtained is exemplified by the existence of flexible, resilient Ethyl Rubber [50–50 mixture of ethyl cellulose and such plasticizers as chlorinated biphenyl, tricresyl phosphate, Herculyn (methyl dihydroabietate), Abalyn (methyl abietate)]; and, at the opposite extreme, a hard, non-deformable product used in the manufacture of golf-balls. However, while products having quite different properties can be obtained by proper compounding of ethyl cellulose, there are certain properties which are characteristic of the base plastic and which may be retained, enhanced or diminished in the final product.

For example, ethyl cellulose exhibits excellent resistance to the passage of an electric current and hence it is widely used as an insulating material. Its breakdown voltage is 3000 volts for a film thickness of 0.001 inch, and the power factor is also low, 0.0025–0.003. Furthermore, there is no decomposition or conductance when it is subjected to arcing over the surface. In addition, these films have excellent flexibility and good water resistance, two factors which are of considerable importance in wire insulation coatings.

The water absorption of ethyl cellulose is 1.25% after 48 hours of immersion at 25° C. It shows good resistance to alkalies and aliphatic hydrocarbons, fair resistance to dilute acids, but is decomposed by concentrated mineral acids and dissolves in most organic solvents.

The mechanical properties of ethyl cellulose are excellent, as shown by an impact strength of 0.6–1.8 (Izod), tensile strength of 6,000–14,000 lbs. per sq. in., elongation of 10–40% and hardness of 71% of that of glass. These mechanical properties, together with its resistance to moisture and cold flow, insure dimensional stability under a wide range of humidity and temperature conditions. An outstanding characteristic of ethyl cellulose films is their excellent flexibility, even when unplasticized, at the temperature of -40°C . See Figure 12.6. This property is extremely important for gaskets,

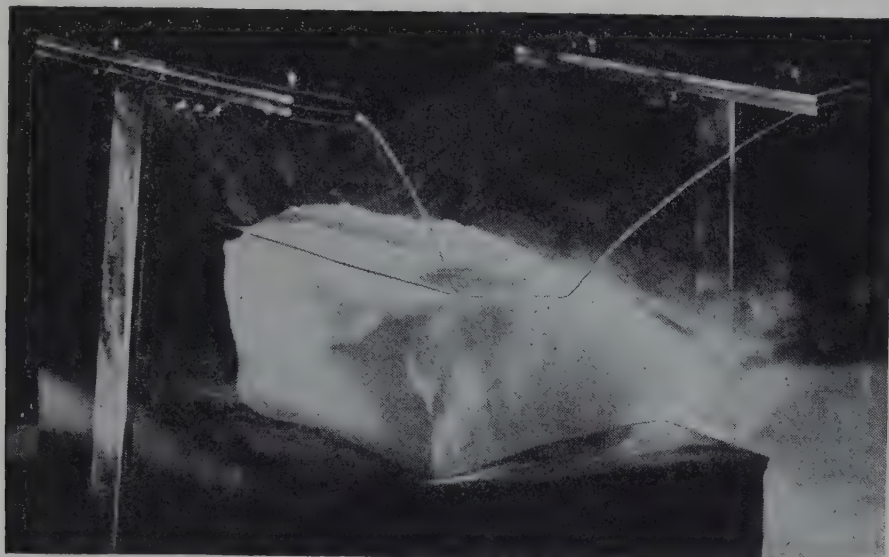


FIG. 12.6. Ethyl cellulose flexing test. A film of ethyl cellulose is flexed resting on a block of dry ice, subjecting the film to extremely low temperatures, showing the ability of the plastic film to resist cracking. (Courtesy Hercules Powder Company.)

fabric coatings and fuel containers which are to be exposed to low temperatures. The relatively high softening point (100 – 130°C .), of the unplasticized material indicates that ethyl cellulose plastics can be used advantageously over a very wide range of temperatures.

Ethyl cellulose is added to waxes in order to increase the toughness and the softening point of the wax. At the same time, the presence of wax improves the water resistance of the ethyl cellulose. Mixtures of ethyl cellulose and waxes or resins may be applied either as hot melts or in solutions. Ethyl cellulose is used in lacquers, varnishes and adhesives in order to improve the toughness, flexibility and hardness of the resulting films.

The low specific gravity of ethyl cellulose (1.14) is an important factor when considering cost, because more molded pieces can be

made from a pound of light plastic than from a pound of heavy plastic. It has been found that ethyl cellulose lacquers give about 45% greater coverage than cellulose nitrate lacquers and about 20% greater coverage than cellulose acetate lacquers when equal weights of the plastics are used.

In its compounded modifications, ethyl cellulose may be used in countless ways. Its applications, at the present time, include packaging papers, wrapping foil, artificial leather, lacquers, adhesives, furniture trim, automotive parts, wire insulation, toilet articles, novelties, fabric coatings and flexible rubber-like tubing. The product is sold by the trade names: Ethocel, Ethofoil, and Hercules Ethyl Cellulose.

The physical properties of the cellulose derivatives discussed above are given in Table V-12.

TABLE V-12. COMPARISON OF PHYSICAL PROPERTIES OF CELLULOSE DERIVATIVES ^a

Properties	Cellulose Nitrate	Cellulose Acetate	Cellulose Acetate-Butyrate	Ethyl Cellulose
Specific gravity	1.35-1.60	1.27-1.37	1.21	1.14
Refractive index N_d	1.50	1.47-1.50	1.47	1.47
Tensile strength, lbs. per sq. in.	6,000-9,000	2,800-10,000	2,800-7,500	6,000-9,000
Modulus of elasticity, lbs. per sq. in. $\times 10^6$	2-4	.6-3.5	2-3.5	2-4
Compressive strength, lbs. per sq. in.	20,000-30,000	11,000-27,000	8,500-22,500	11,000
Flexural strength, lbs. per sq. in.	9,000	5,000-16,000	4,000-13,000	4,000-12,000
Impact strength, ft. lbs. per inch of notch	2.0-8.0	.7-.42	.8-5.5	.6-1.8
Hardness, Brinell, 10 kg., 2.5 inch ball	8-11	8-15	10	—
Thermal conductivity 10^{-4} cal. per sec. per cm. per $^{\circ}$ C.	3.1-5.1	5.4-8.7	4.5-7.8	3.8-6.3
Thermal expansion $\times 10^{-5}$ in. per in. of length per $^{\circ}$ C.	12.0-16.0	14.0-16.0	11.0-14.0	10.0-14.0
Safe operating temperature $^{\circ}$ F.	140	140-180	140-200	140-200
Softening point $^{\circ}$ F.	160	122-205	140-250	210-265
Distortion under heat $^{\circ}$ F.	150	122-212	140-200	130-150
Cold flow	slight	slight	slight	slight
Dielectric strength, volts per mil	300-780	350-400	250-400	400-700
Power factor, 10^6 cycles	.074-.100	.035-.060	.010-.050	.007-.030
Water absorption, per cent by weight in 24 hours	1-3	2.1-6.9	1.2-2.0	1.25 (48 hrs.)
Elongation per cent	10-40	15-80	8-82	10-40

^a A Ready Reference for Plastics, 1943 Edition, Boonton Molding Company, Boonton, N. J.

REGENERATED CELLULOSE

Regenerated cellulose is the name given to the product obtained by first plasticizing cellulose by dissolving either cellulose or a suitable derivative of cellulose in a solvent and then deplasticizing the cellulose by causing precipitation of the cellulose in a suitable bath. For example, in the cuprammonium process for making rayon, cellulose is dissolved in an ammoniacal solution of cupric oxide. The viscous solution obtained is filtered, forced through very fine holes in a spinneret into water, the thread stretched and then led into an acid solution where coagulation is completed.

In the viscose process, which accounts for approximately three-fourths of the rayon produced and which is also the method used in making cellophane, the cellulose is first changed to cellulose xanthate before dissolving in a suitable solvent. In making cellulose xanthate, a purified wood pulp (see Chapter IX) is pressed into sheets which are steeped in an 18% solution of sodium hydroxide at 18° C. The pure alpha cellulose swells in the alkaline solution and the product is known as soda-cellulose. The excess alkali is squeezed out and the sheets are shredded to form the "crumb." This "crumb" contains one molecule of sodium hydroxide for every two glucose anhydride units present in cellulose. The soda-cellulose is stored at room temperature for three days, out of contact with air. During this aging process, there is some oxidation (from the entrapped air) and also some degradation of the micellar structure of the cellulose.

The aged soda-cellulose is then mixed with carbon disulfide, forming cellulose xanthate which is dissolved in sodium hydroxide solution. This viscose solution is stored in tanks, out of contact with air for three or four days at a temperature of 19° C. During this "ripening" process a gradual hydrolysis of the cellulose xanthate occurs. At first, the viscosity of the solution decreases due to the dispersion of the larger particles to smaller particles. As the hydrolysis proceeds, however, the viscosity gradually increases, the increase being rather rapid as the solution approaches the optimum state for spinning. When the ripening process is complete (determined by empirical tests) the solution is de-aerated by evacuating the space above the solution, filtered, and then spun by forcing it through tiny orifices in a spinneret. The spinneret leads directly into a bath of sulfuric acid and sodium sulfate where the cellulose is coagulated in the form of continuous filaments. The bath temperature is kept at 45° C. The holes in the spinneret are of the order of 0.08 mm. in diameter and there may be from 10 to 150 openings in



FIG. 12.7. Beginning of the actual making of "Cellophane" cellulose film. A sheet of "Cellophane" is seen leaving the coagulating bath on its way through a series of chemical treatments toward the finished product. (Courtesy du Pont Company.)

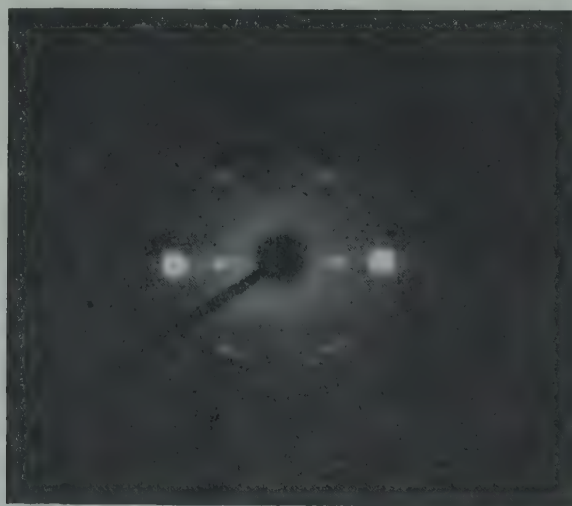


FIG. 12.8. X-ray diagram of Fortisan.

each spinneret depending on the ultimate thickness of the thread to be formed. The threads are wound on a bobbin, washed with sodium carbonate solution, bleached with chlorine, washed again and dried. To make sheets of cellophane, the viscose solution is extruded through a very narrow slit into the acid bath, and subsequent treatment is similar to that used for rayon threads. After removal of sulfur and bleaching, cellophane sheets are passed through a glycerine bath in order to make them flexible. Figure 12.7 illustrates the formation of a cellophane sheet.

A regenerated cellulose product having a high tensile strength, up to 7 g. per denier, is obtained by the hydrolysis of cellulose acetate. In this process, a dilute aqueous alkali solution is used as the hydrolyzing medium. The threads may be passed through the alkaline solution under tension or they may be stretched, wound on a bobbin while still stretched and the whole mass hydrolyzed. In order to decrease the amount of swelling which would normally occur in the alkaline medium, anti-swelling agents such as sodium tartrate and sodium lactate may be added to the solution. The hydrolysis of the cellulose acetate may be partial or complete. It is interesting to note that products have been obtained which can be dyed by both cellulose acetate dyes and cellulose dyes. The trade name of this regenerated cellulose is Fortisan. Figure 12.8 shows the x-ray diagram of the commercial product. The high degree of crystallinity which is introduced by stretching the cellulose acetate prior to hydrolysis, persists in the hydrolyzed product. This is undoubtedly the cause of the high tensile strength of Fortisan.

Review Questions

1. By means of structural formulas, show the relationship which exists among the more important derivatives of cellulose.
2. What factors are involved in the variation of properties of the cellulose derivatives?
3. What precautions must be taken in the manufacture and fabrication of cellulose nitrate?
4. How does the fabrication of cellulose nitrate differ from that of other types of cellulose derivatives?
5. What part does each of the following play in the compounding of cellulose nitrate for coatings:
 - (a) base resin
 - (b) diluent
 - (c) plasticizer
 - (d) evaporation rate of solvent?

6. Compare the advantages, disadvantages, typical applications and fabrication methods of the important cellulose esters.

7. How is the acetyl content of a cellulose acetate plastic best regulated?

8. What methods are available for varying the flow characteristics of molding powders?

9. What plasticization and deplasticization methods are used in the preparation of "acetate rayon"?

10. What is the principal desirable property and the principal undesirable property of each of the cellulose esters?

11. What is the Williamson reaction?

12. What compounding agents are used with ethyl cellulose in moldings or coatings?

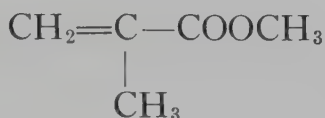
13. Why is the choice of solvent or solvent blend in ethyl cellulose coatings of importance?

14. Show, by a flow chart, the steps involved in the preparation of viscose rayon.

CHAPTER XIII

SYNTHETIC PLASTICS IV: ACRYLIC RESINS

Probably no other synthetic resins appeal to the layman more than the optically-clear, glass-like products which are representative of the acrylic family. The most popular member of these structurally-similar acrylic resins is that obtained from methyl methacrylate:



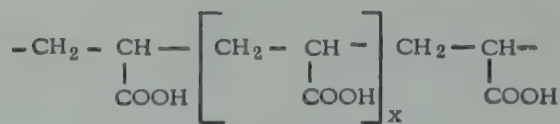
The plastic product produced from this monomer is better known in industry by the trade names of Lucite, Plexiglas, Crystallite, and Acryloid.

Plastic products of this nature first became of interest as a result of Röhm's work in 1901. They were not produced commercially, however, until about 1931 when the Röhm & Haas Co. first manufactured them in the form of coating materials and bonding agents. A little later, the pre-fabricated sheets and molding materials known respectively as Plexiglas and Crystallite were marketed. About the same time, the plastic polymer was also placed on the market by the E. I. du Pont de Nemours Company. The entrance of this product into the plastics industry was greeted with enthusiasm, particularly because of its transparency and light conductance. The rapid growth of the industry has continued as acrylic resins are constantly being introduced into new fields such as advertising, dentures, optical instruments, safety glass and aircraft cockpit enclosures.

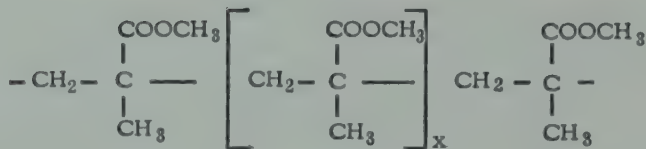
Actually, the acrylic family embraces all products formed by the polymerization of monomers which are, in effect, derivatives of acrylic acid.



Thus, polyacrylic acid, polymethylacrylic acid, polybutyl methacrylate, and polymethyl methacrylate are all structurally related:



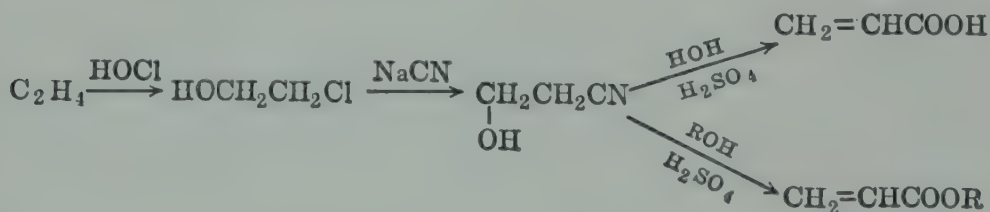
polyacrylic acid



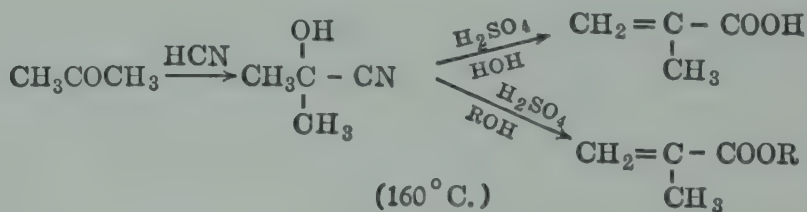
polymethyl methacrylate

The polymerized acids and their esters thus constitute an important group of plastic products.

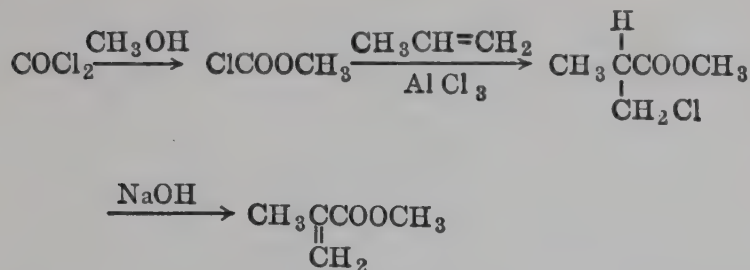
The preparation of the polymer consists of an addition polymerization of the proper monomer. The acrylate monomers may be prepared from ethylene cyanohydrin, which is made from ethylene. The following scheme represents the reactions involved in the preparation of acrylate monomers:



The methacrylate monomers are obtained from acetone, hydrogen cyanide and the proper alcohol, according to the following reactions:



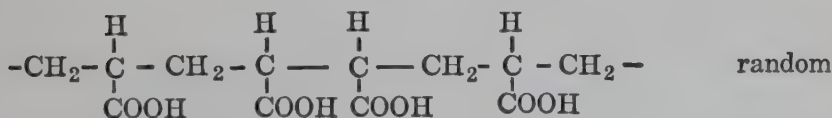
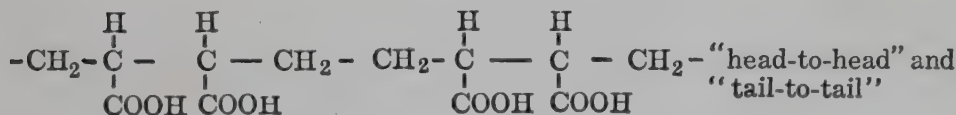
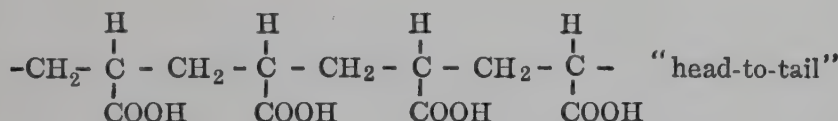
Various other methods have been employed to prepare the unsaturated esters. An interesting method is the catalytic removal of hydrogen chloride from methyl α -chloroisobutyrate, $(\text{CH}_3)_2\text{CClCOOCH}_3$, using anhydrous ferric chloride as the catalyst. Another process which has been patented is represented by the following reactions:



It is interesting to note that the monomeric methacrylate esters may be obtained by the thermal decomposition of the polymeric esters. At 400° C., the depolymerization is rapid and complete.

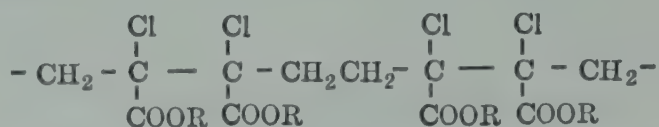
Other derivatives which can be polymerized are: α -halo acrylic acids or esters, acrylonitrile, acrylyl halides, amides, anhydrides and anilides. Aside from a variable but slight degree of branching or cross-linking which may occur, the polymers consist of simple linear molecules.

Three methods of combination of the monomeric units are possible:



Most of the experimental work which has been done on the problem of determining the exact structure of the chains of vinyl polymers indicates that they have a "head-to-tail" arrangement. (Since this work has been done chiefly with polystyrene and polyvinyl compounds, the discussion of the evidence will be found in chapters XIV and XV.) The only exceptions to the "head-to-tail" arrangement which have been found to date are the polymers obtained from alkyl α -halogen acrylates. These are believed to have a head-to-head, tail-to-tail arrangement. Evidence for this arrangement is found in the fact that the α -haloacrylate polymers react with potassium iodide at room temperature to liberate iodine. They also are completely dehalogenated when treated with zinc. Both of these reactions are

characteristic of 1,2-dihalides and indicate the following structure for the polymer:



Polymerization.—Since polymethyl methacrylate is the most important member of the acrylate family, this discussion will be concerned principally with the polymerization of methyl methacrylate. The actual polymerization may be carried out by any of the following methods: mass reaction, photochemical polymerization, emulsion polymerization or solution polymerization.

1. Mass Reaction. Polymerization of undiluted monomer at an elevated temperature and in the presence of a catalyst results in a tough, elastic product which dissolves with difficulty. In the polymerization of acrylic acid, a solid polymer is slowly deposited from the excess liquid monomer. This is unlike most polymerizations of vinyl monomers. Generally, the polymer is soluble in the excess monomer and forms a gel. The most frequently used catalyst for the polymerization of the acrylic monomers is benzoyl peroxide. The polymerization may be carried out either with or without plasticizers. Some of the best plasticizers for use with polymethyl methacrylate are: dibutyl phthalate, dibutoxyethyl phthalate, chlorinated biphenyl, butyl phthalyl butyl glycolate, *p*-tolylethyl sulfonamide and tricresyl phosphate. Fillers are rarely used with polymethyl methacrylate because they would detract from the excellent transparency of the polymer. The two principal difficulties involved in the mass polymerization of methyl methacrylate and related compounds are: (1) the tendency of bubbles to form as a result of the exothermic nature of the reaction and the trapping of these bubbles by the viscous fluid formed by partial polymerization, (2) the tendency of the material to shrink during polymerization. In this connection, it is interesting to note that the specific gravity of methyl methacrylate is 0.936 at 20° C., and the specific gravity of polymethyl methacrylate is about 1.186 at 20° C. The specific gravity of the polymer varies somewhat, depending upon the completeness of polymerization. Thus, there is a volume shrinkage of approximately 21% when the polymer is made from the monomer. If the polymer is to be pulverized for use in the molding process, neither of these difficulties is important. However, if a clear, transparent cast object is desired, free from any trapped bubbles, the monomer must be polymerized under carefully controlled temperature conditions, pref-

erably below 80° C. In order to overcome the difficulty of shrinkage within the mold, a thin layer of methyl methacrylate can be polymerized in the mold by heating to 70–80° C., for about 24 hours. A second thin layer of monomer is then placed on the solid polymer and this is polymerized. The process can be repeated until the mold is completely full of polymerized methyl methacrylate.

An ingenious method of carrying out a continuous polymerization is to keep half of the mold cold by spraying cold water on it while keeping the other half hot by spraying hot water on it. An insulating strip can be placed around the middle of the mold. A plug of polymerized polymethyl methacrylate is placed in the hot portion of the mold and held in position by a suitable abutment. The liquid monomer is forced into the cold portion of the mold under pressure of nitrogen. The liquid softens the end of the plug and then the plug is gradually withdrawn (about one inch per hour) from the hot end of the mold. As the liquid enters the hot portion of the mold, it polymerizes. A firm undetectable bond is formed between the original plug and the newly polymerized material. By proper control of the temperature, no bubbles are trapped in the polymer and because of the constant pressure of the liquid monomer against the polymerizing surface, there is no shrinkage away from the walls of the mold. It is obvious that such a process can be utilized to manufacture bars, rods or tubes of indefinite length.

In order to speed up the casting of methyl methacrylate, a syrupy solution of the polymer dissolved in the monomer may be introduced into the mold and polymerized by means of heat and a catalyst.

2. Photochemical Polymerization. It has been found that light of certain wave lengths will cause activation of the monomeric acrylates and thus induce polymerization. This method of polymerization has been carried out with undiluted monomer in both the liquid and the gaseous state. Gaseous polymerizations were found to be particularly sensitive to various inhibitors, especially oxygen. The activated unit which is responsible for the initiation of chain growth is apparently destroyed by the oxygen present.

3. Emulsion Polymerization. The water-insoluble monomeric acrylic derivatives may be emulsified and then polymerized. This method depends upon the presence of emulsification agents, regulators, and catalysts as discussed on page 35.

4. Solution Polymerization. The monomer may be diluted with an inert solvent and then polymerized. Examples of typical solvents

which may be used include benzene, dioxan, acetone, alcohol, butyl acetate, ethylene dichloride and methoxyethanol. It has been found that good control of the polymerization reaction can be obtained by this method. Some interesting work has been reported by Strain¹ concerning the effect of various factors involved in the rate of solution polymerization of methyl methacrylate. It should be emphasized here that the rate of polymerization refers to the rate at which monomer is converted to polymer. The actual polymerization, i.e., chain growth, is probably very rapid and rarely measurable, but the rate of conversion of monomer to polymer can be determined.

The results of Strain's experiments may be summarized as follows:

1. *Temperature.* The effect of temperature is similar to its effect in mass polymerization, i.e., the higher the temperature the faster the rate of polymerization and the lower the molecular weight of the product.

2. *Catalyst.* Increasing amounts of catalyst (benzoyl peroxide) also cause an increase in the rate of polymerization and a decrease in the molecular weight of the polymer formed. However, the results are not directly proportional to the amount of catalyst used.

3. *Concentration.* The variations of molecular weight with polymerization temperature and with different concentrations of catalyst are shown graphically in Figure 13.1. The higher the concentration of monomer in solution (at least up to 50%), the more rapid the polymerization and the higher the molecular weight of the polymer formed. The rate of polymerization of three different concentrations of methyl methacrylate in benzene is shown graphically in Figure 13.2.

4. *Solvent.* The nature of the solvent has an important effect upon the polymerization rate and also upon the molecular weight of the polymer. Figure 13.3 represents the rate of polymerization of 20% solutions of methyl methacrylate in five different solvents.

Variations in the composition of the monomer cause different rates of polymerization and marked differences in the properties of the polymers formed. The esters of acrylic acid polymerize at a much faster rate than those of methacrylic acid under the same experimental conditions. As might be expected, esters formed from

¹ Strain, *Ind. Eng. Chem.* **30**, 345 (1938).

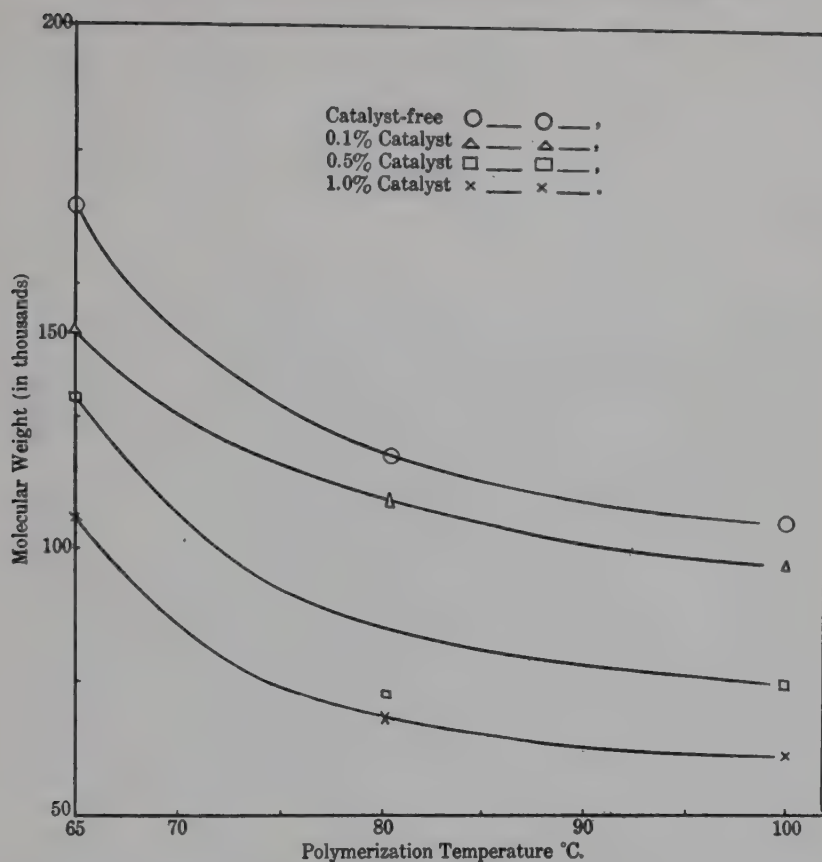


FIG. 13.1. Variation of molecular weight with polymerization temperature. (Strain, *Ind. Eng. Chem.* 30, 346, 1938.)

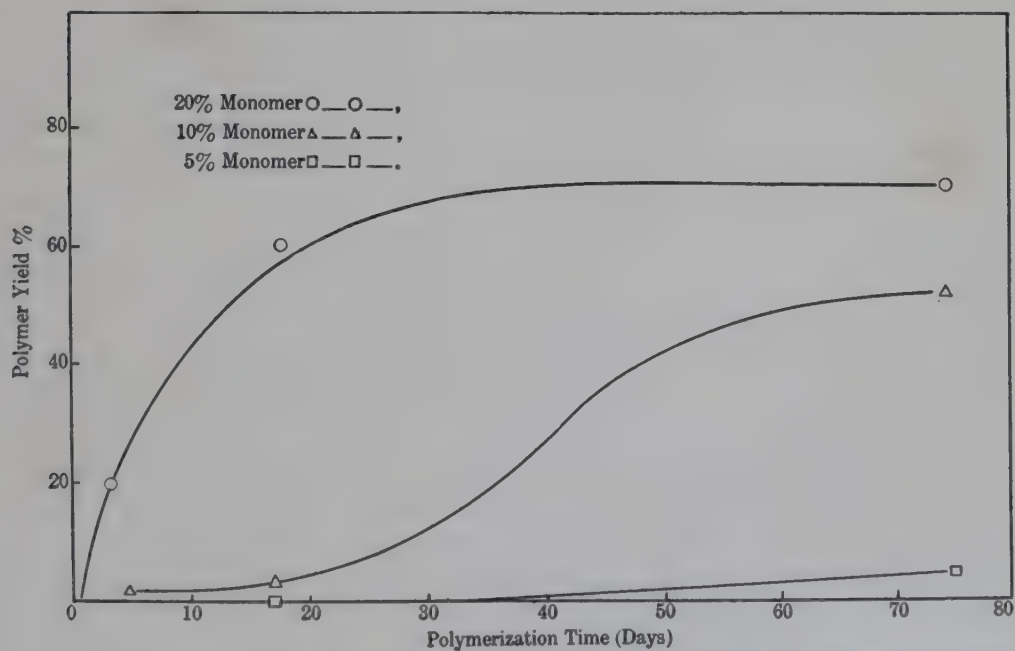


FIG. 13.2. Polymerization rate of methyl methacrylate in benzene at 65°C. (Strain, *Ind. Eng. Chem.* 30, 346, 1938.)

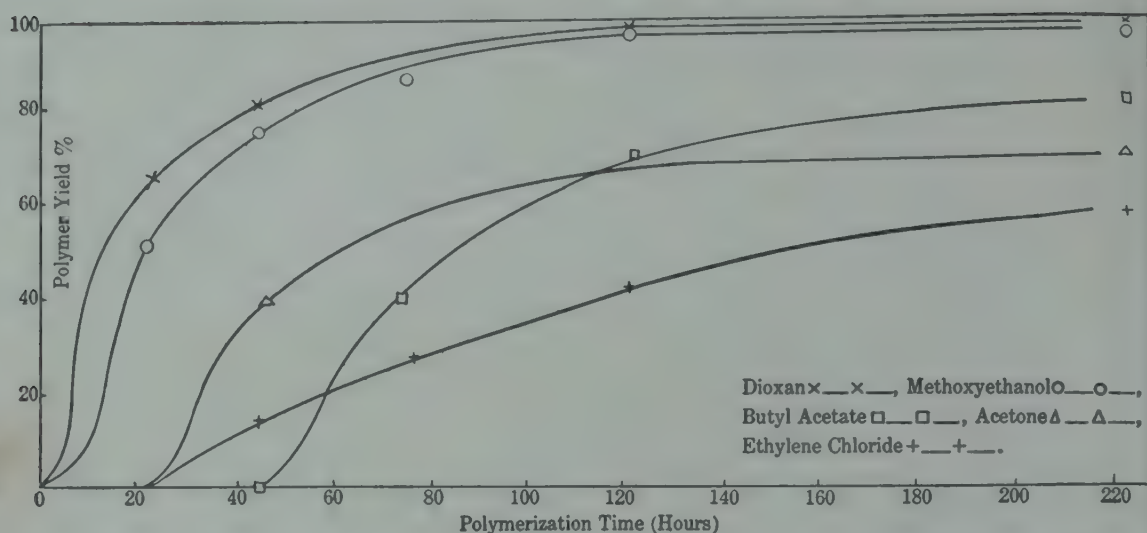


FIG. 13.3. Polymerization rate of methyl methacrylate in 20% solutions at 65° C. (Strain, *Ind. Eng. Chem.* **30**, 347, 1938.)

the higher molecular weight alcohols polymerize more slowly than those obtained from low molecular weight alcohols.

Compounding and Fabrication.—The variability of the production methods permits the marketing of the acrylic resins in a variety of forms both pre-fabricated and completely unfabricated. The plastic material, for example, is available in molding powders of many desirable meshes and a wide range of softening points. It should be pointed out that the methacrylate polymers do not melt to a liquid state readily, but possess a rubbery consistency over a wide temperature range. The fluidity can be increased and the rubber-like characteristics decreased by blending the methacrylate polymer with other resins, such as ester gum, dammar, rosin and coumarone-indene resins. Such blended products are useful in hot-melt applications. Other materials which can be blended with methacrylate polymers are cellulose nitrate, cellulose propionate, certain phenol-formaldehyde and alkyd resins, vinyl chloride-acetate copolymers, chlorinated rubber and chlorinated biphenyl. The softening point and the fluidity of all acrylate polymers can be controlled by varying the nature and amount of plasticizer used. For compression molding of these resins, temperatures of 150–190° C. are used, along with pressures of 3000–7000 lbs. per sq. in. Although a softer resin is generally used for injection molding, higher temperatures, 200–260° C., and high pressures, 10,000–30,000 lbs. per sq. in., are necessary for satisfactory performance.

The base resin is available commercially in the form of granular solids, adaptable to other fabrication methods such as coatings or

castings. These base resins are also marketed in the form of solutions or emulsions. The best solvents for the preparation of solutions are esters and ketones.

Finally, pre-fabricated forms of molded or cast sheets, rods and tubes may be used for further processing of the methacrylate polymers. The products are available in these forms having any desired



FIG. 13.4. Shaping Plexiglas sheet on a form.
(Courtesy Röhm & Haas Co., Inc.)

color, various degrees of plasticization and different softening points. From these pre-fabricated forms, more complex shapes may be obtained by proper machining and designing. The methacrylate resins can be sawed, cut, carved, turned, drilled, swaged, cemented together and polished. One of the simplest and most interesting uses of acrylate sheets is to first soften them by the application of heat (200° F.), then shape them by bending them over wooden forms, finally allowing them to cool while still on the forms. This method is used in the formation of a bomber nose.

The shaping of the plastic on a suitable form is illustrated in Figures 13.4 and 13.5, and the trimming of the shaped article is illustrated in Figure 13.6.

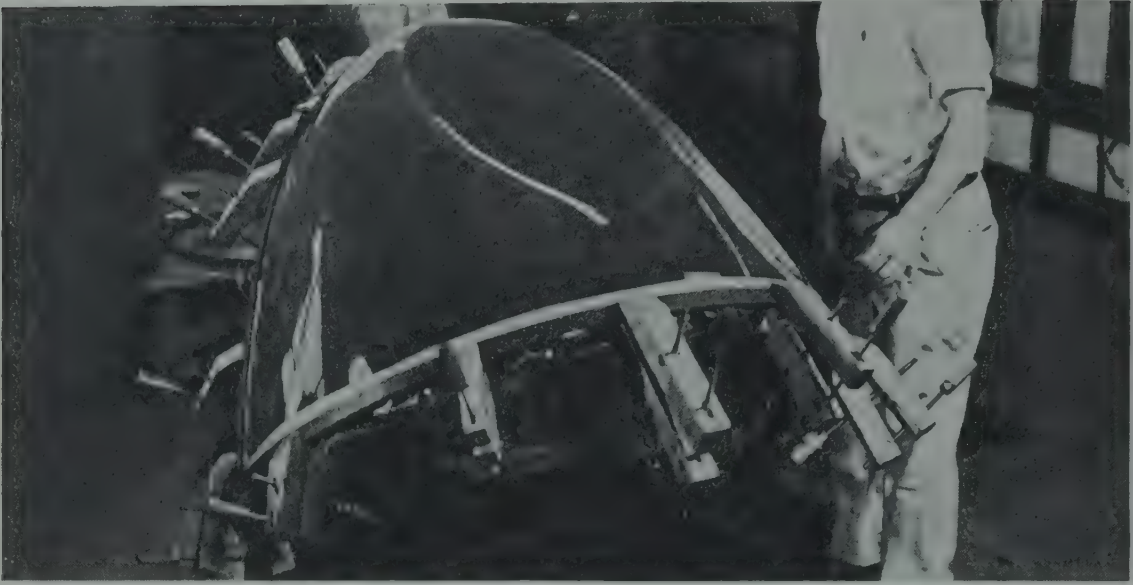


FIG. 13.5. The shaped Plexiglas sheet is allowed to cool while clamped in position.
(Courtesy of Röhm & Haas Co., Inc.)

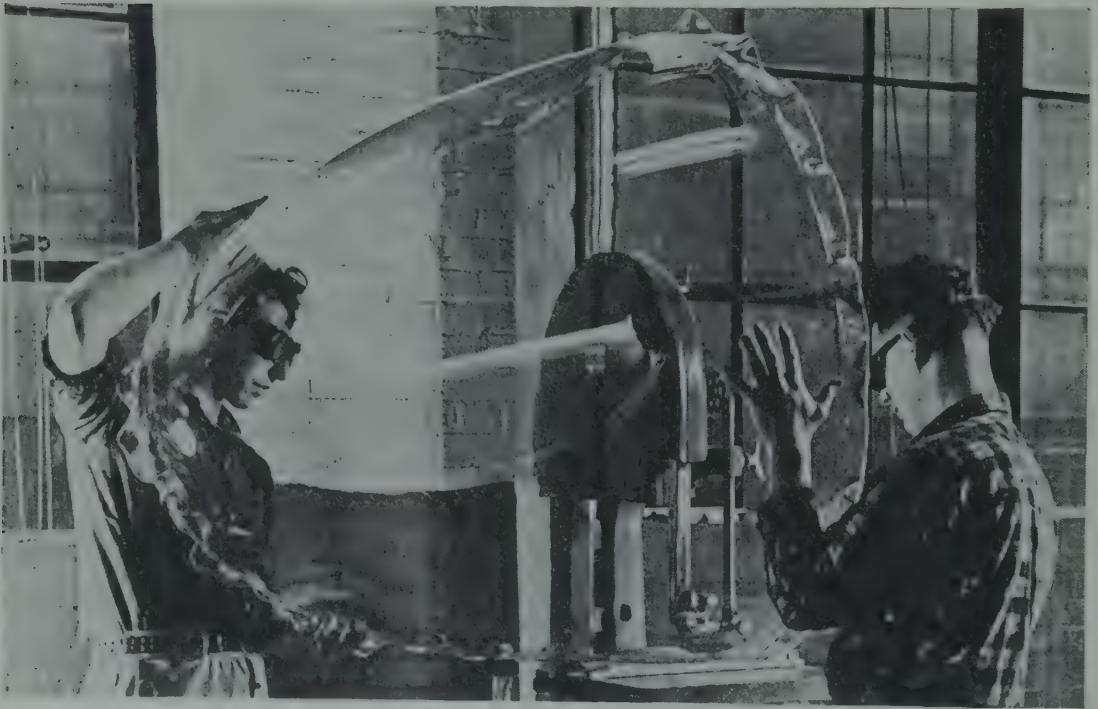


FIG. 13.6. Trimming edges of Plexiglas nose section.
(Courtesy of Röhm & Haas Co., Inc.)

Recent developments indicate that more rapid and more accurate shaping of semi-spherical products may be accomplished by a vacuum forming technique. In this process, the heat-softened (250° F.) sheet of polyacrylate is placed over the top of a chamber and clamped into position so that the contact between the polyacrylate sheet and the chamber is air tight. At the bottom of the chamber is a valve connected to a vacuum line. When this valve is opened, a partial vacuum is created in the chamber and the sheet is drawn into a semi-spherical shape. A contact point may be placed at any desired depth so that when the sheet reaches it, the valve is closed automatically. If the sheet retracts during cooling, the valve is automatically opened and the desired shape is recovered.

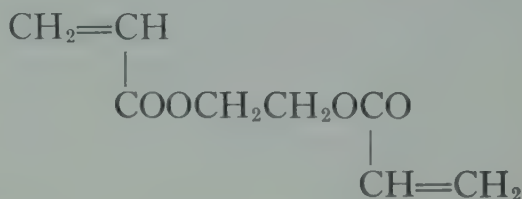
A further development of the vacuum technique is known as "snap-back forming." This process is based upon the fact that a flat polyacrylate sheet which has been deformed tends to revert to its original flat state when the cause of deformation has been removed, provided, of course, that the sheet has not cooled sufficiently to set. In "snap-back forming" a semi-spherical shape is produced by the vacuum technique. However, instead of allowing the sheet to cool in this position, a mold is lowered into the cavity or "bubble" and air is gradually allowed to enter the chamber. As the sheet tends to snap back to its original flat form, it takes the shape of the mold and is allowed to cool in this position. These processes of vacuum forming and snap-back forming have been of great value in accelerating the production of certain aircraft parts.

Properties and Applications.—The properties of the polyacrylates and polymethacrylates vary from hard, tough solids to semi-liquids, depending upon the particular ester used for the polymerization. The solid polymers obtained from methacrylates are much harder than those obtained from the corresponding acrylates. For example, polymethyl acrylate is a rather soft solid, while polymethyl methacrylate is so hard that it can be sawed, drilled and turned satisfactorily.

A comparison of the properties of the polyacrylic acid esters shows some interesting relationships.² Although polymethyl acrylate is soft, when compared with polymethyl methacrylate, it is very tough, and a film of it can be stretched 1000% before it breaks. Polyethyl acrylate is softer, and more elastic, but not as tough. The polymer obtained from the *n*-butyl ester is quite soft and feels sticky when touched, while the octyl and lauryl polymers are extremely soft and tacky. The polymers obtained from the esters of

² Neher, *Ind. Eng. Chem.* **28**, 269 (1936).

the isomeric butyl alcohols exhibit increasing hardness in going from *n*-butyl to isobutyl to sec.-butyl to tert.-butyl. The normal, iso and secondary polymers are all elastic and pliable, but the tertiary butyl polymer exhibits very little pliability and is a hard, tough, almost brittle solid. It was stated earlier that the methacrylate polymers are harder than the corresponding acrylate polymers. Furthermore, in both series, as the molecular weight of the alcohol used in making the ester increases, the hardness of the polymer formed decreases. It is interesting to note that the *n*-amyl methacrylate polymer is about as soft as polymethyl acrylate. Polycyclohexyl acrylate is hard and tough, but poly-*n*-hexyl acrylate is soft and tacky. The polymer obtained from ethylene glycol diacrylate is hard, infusible, and insoluble in organic solvents. An examination of the formula for the monomer



reveals the possibility of the two vinyl groups of one molecule participating in the growth of two chains, thereby causing cross linkage and consequently decreasing the solubility in organic solvents. Polymerization of acrylic acid amide results in the formation of a cross-linked polymer, due to the loss of ammonia from two amide groups on adjacent chains. The cross-linkage consists of an imide group and the product is horn-like. Acrylonitrile can also be polymerized to form a cross-linked polymer³ which is insoluble in typical organic solvents.

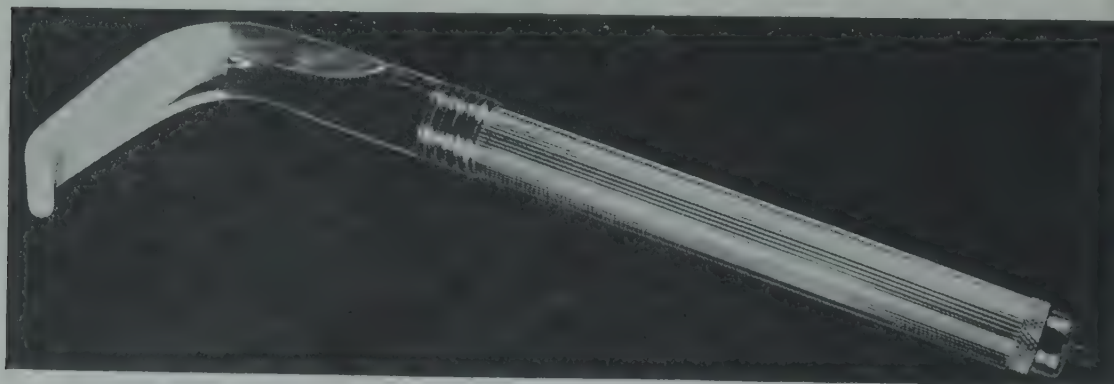


FIG. 13.7. Edge lighted surgical instrument made from polymethyl methacrylate. (Courtesy of Röhm & Haas Co., Inc.)

³ Kern and Fernow, *J. Prakt. Chem.* **160**, 281–295 (1942).

The best known polymer in this family is polymethyl methacrylate. Its most outstanding property and the one which is of greatest interest to plastics fabricators is the crystal-clear transparency of the plastic. High internal reflection and transmission of light which enters from any source results in the so-called "piping effect." Due to this, light may be transmitted from the source and "piped" by the plastic to a roughened surface at the other end of the rod. At this surface the light emerges from the plastic with only a slight loss of intensity. Such a feature is of value in making surgeon's lights, advertising displays, and decorative novelties. See Figures 13.7 and



FIG. 13.8. Light "piped" from a concealed source by polymethyl methacrylate. (Courtesy of Röhm & Haas Co., Inc.)

13.8. The high internal reflection is the basis for the increasing use of polymethyl methacrylate as reflectors to mark the edge of a highway. The excellent transparency of this plastic is of value in the making of lenses and windows, especially for airplanes. The high degree of transparency of polymethyl methacrylate resin is responsible for its use in the preservation of various specimens. The specimens are embedded by a process of gradually building up separate layers of the plastic as described on page 243. The preservation of an ear of corn and a human mandible are shown in Figures 13.10 and 13.11. In addition to the exceptional optical properties, the methacrylate resins

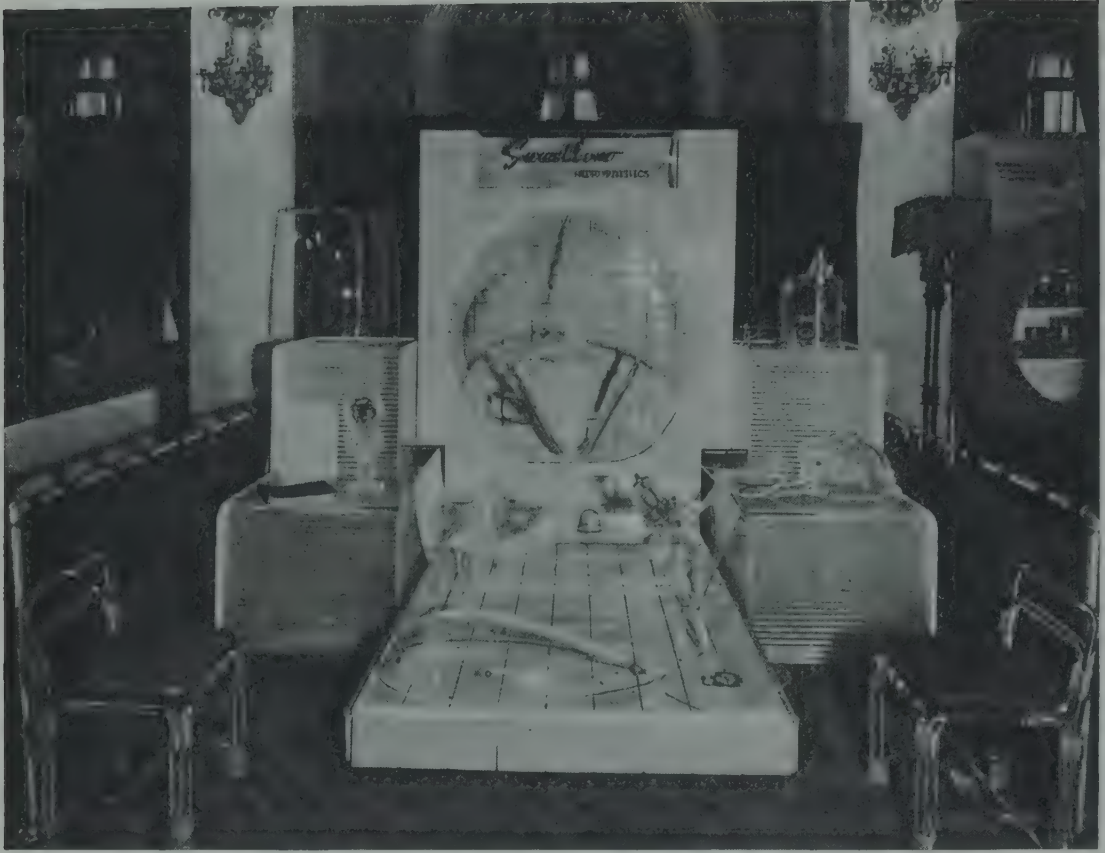


FIG. 13.9. The versatility of application and the beauty of design possible with polymethyl methacrylate resins are shown in the above illustration. (Courtesy of Swedlow Aeroplastics Corporation.)

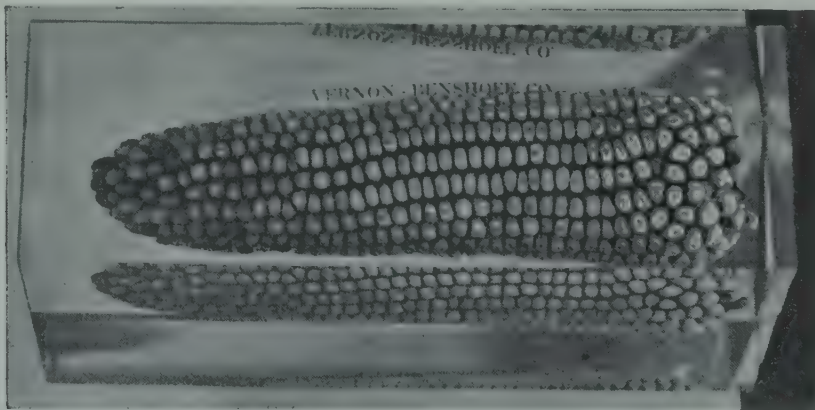


FIG. 13.10. Ear of corn embedded in polymethyl methacrylate. (Courtesy of Vernon-Benshoff Company.)

are only approximately half as heavy as ordinary glass. The low specific gravity is of definite advantage from the viewpoint of both the manufacturer and the consumer. The light weight, for example, is of great importance in the acceptance of acrylate resins in the aircraft industry.

Of definite desirability, also, are the two factors of mechanical strength and surface hardness associated with polymethyl methacrylate. The mechanical strength of these resins is illustrated by satisfactory values for impact resistance (0.2–0.3 foot-pounds, Charpy method), flexural strength (12,000–14,000 lbs. per sq. in.), tensile strength (9,000–12,000 lbs. per sq. in.), and hardness (17–20, Brinell, using force of 500 kg. on 10 mm. ball).

An interesting sidelight of the impact or shock resistance is the fact that, when shattered, the acrylate sheeting breaks into dull-edged pieces which are not particularly dangerous. Although lower than the hardness values of polystyrene and urea-formaldehyde resins, the surface hardness is sufficient to resist most forms of abrasive action. Furthermore, minor scratches and surface disfigurements may be removed by polishing, buffing, and waxing operations.

The resistance of polymethyl methacrylate to the passage of an electric current is good. The plastic exhibits high dielectric strength and is of particular interest because there is no charring or carbonization when it is subjected to an electrical flash over the surface. Although the power factor is not as low as that of polystyrene, it is low enough (0.02–0.03 for a 10^6 cycle) so that the plastic is a satisfactory insulating material.

Depending upon the nature and amount of plasticizer used, the water absorption of cast or molded polymethyl methacrylate may be as low as 0.3–0.4% when immersed for 24 hours at 25° C. This factor, together with the excellent resistance of the plastic to all kinds of weathering make Plexiglas and Lucite acceptable for the most specialized types of aircraft windshields and dials, as well as for numerous other purposes where clarity of vision and dimensional stability under all sorts of climatic conditions are desirable. An

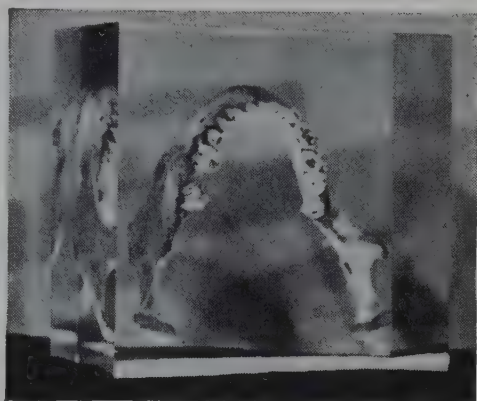


FIG. 13.11. Human mandible embedded in polymethyl methacrylate. (Courtesy of Vernon-Benshoff Company.)

important use of acrylate polymers is the making of dentures (Figure 13.12).

Polymethyl methacrylate exhibits excellent resistance to salt solutions, acids (other than oxidizing acids), alkalies, mineral, animal and vegetable oils, and good resistance to aliphatic hydrocarbons. It dissolves in aromatic hydrocarbons, esters and ketones. When ignited, it burns slowly with a luminous flame.

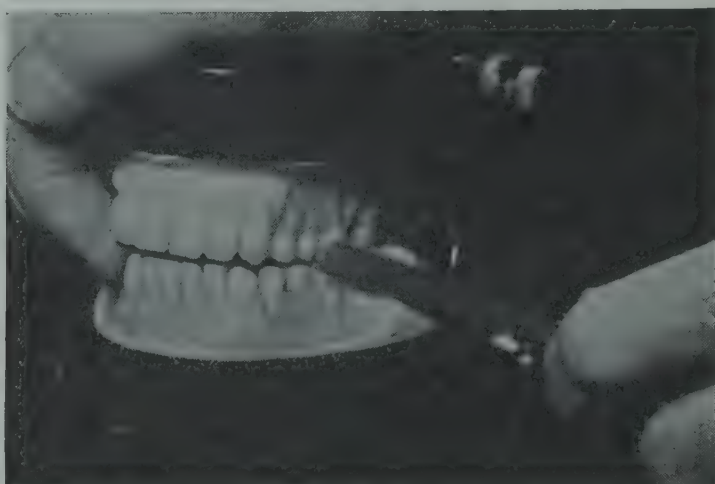


FIG. 13.12. The hardness of a Plexiglas denture is illustrated by "biting" through a pencil. (Courtesy of Röhm & Haas Co., Inc.)

The softening points of molded and cast objects made from polymethyl methacrylate vary from 60–115° C. Products made from the "soft" injection molding powder soften at 60–82° C., those made from the "hard" compression molding powder soften at 82–88° C., while cast products soften at 88–115° C. Resins with a softening point above the boiling point of water are necessary for surgical applications where the instrument must be sterilized.

One of the most interesting applications of the acrylate polymer is its use in the fabrication of shock-proof glass, Plexite.⁴ The technique, in this case, involves the use of a solution or colloidal dispersion of the polymer in ethylene dichloride. The viscous polymer blend is first added to pressure kettles which are partially evacuated. It is then heated to eliminate air bubbles and produce the desired viscosity. After filtering, the solution is spread on both plates of glass which are to be bonded to produce the safety glass. The spreading is done by the use of a trough immediately above the glass surface. The plate of glass is conveyed under the trough and

⁴ *The Glass Industry*, 19, 83 (1938).

the amount of material deposited is regulated by variation of the speed of the conveyor, the width of the opening in the trough, and the depth of the material maintained in the trough. The plastic layer is dried at a temperature just below the boiling point of the solvent. The glass surfaces are then ready to be bonded into the Plexite sandwich. To insure perfect optical characteristics, the plates are examined for bubbles. If any bubbles occur, they are broken and filled with the contacting agent. The surfaces are then sprayed with a contacting agent and pressed together. The glass sandwich is then passed through a heavy rubber wringer and cooled while under pressure.

TECHNOLOGY OF RESIN EMULSIONS AND DISPERSIONS

Since the acrylate resins are often used as waterproofing agents or coatings in the form of resin emulsions, the preparation and application of these resin emulsions will be described here. When salt or sugar is dissolved in water, the solid particles are dispersed in the liquid in the form of ions or molecules, and the resulting solution is referred to as a true solution or a molecular dispersion. Some of the outstanding characteristics of a true solution are that the dissolved particles exert a marked effect in lowering the freezing point of the solution, raising the boiling point of the solution and causing the development of osmotic pressure. These properties are frequently called the colligative properties of solutions, because they are dependent upon the number of dissolved particles rather than the chemical nature of the dissolved particles.

On the other hand, when finely powdered dirt or diatomaceous earth or some other water-insoluble material is suspended in water, a more or less homogeneous mixture can be maintained by rapid agitation, but when the mixture is allowed to stand, the insoluble material separates, sometimes rapidly, sometimes slowly. Such a mixture is known as a coarse suspension or coarse dispersion. The coarsely suspended material has no effect on the colligative properties.

The size of the particles in true solution is believed to be $< 1 \text{ m}\mu$, while the size of particles in coarse suspension is believed to be $> 500 \text{ m}\mu$. In between these two extremes lies the domain of colloid chemistry. These colloidal particles exert little or no effect on the colligative properties mentioned above in connection with true solutions.

The three classes of dispersions may be distinguished by means of filter paper and a semi-permeable membrane, such as a collodion or

parchment membrane. The particles in true solution and in colloidal solution will pass through ordinary filter paper while particles in coarse suspension will be retained by filter paper. Particles in true solution will pass through a semi-permeable membrane while particles in colloidal solution will not pass through such a membrane.

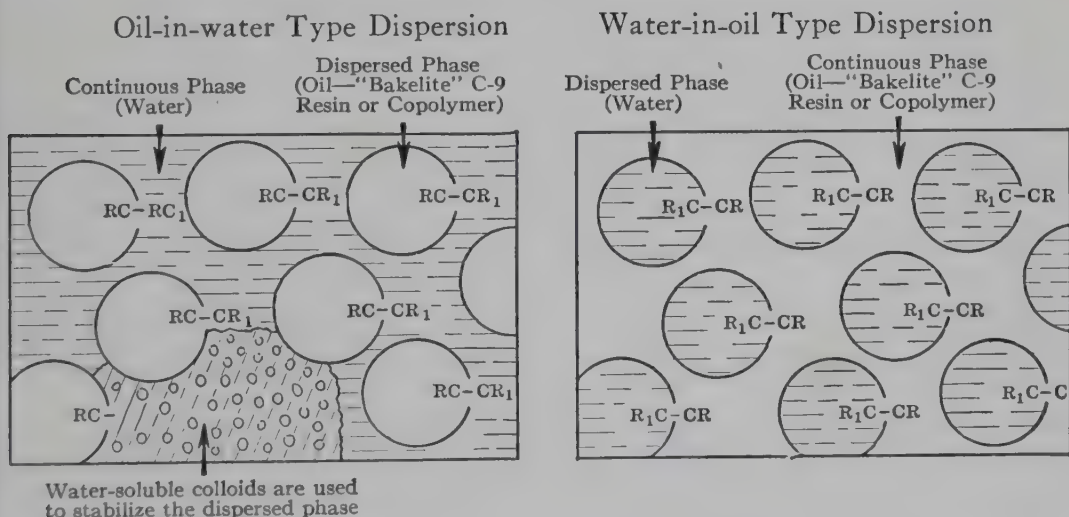
Such materials as starch, gelatin, agar-agar, casein, clays and some polymeric substances, both natural and synthetic, will form colloidal solutions. Free-flowing colloidal solutions are known as sols and if water is the dispersion medium, they are referred to as hydrosols. Upon cooling or partial evaporation, the sol may be transformed to a solid or gel form.

In order to improve the stability and aging characteristics of colloidal dispersions, protective colloids such as soaps, gelatin, glue or casein may be added. Some attachment of the stabilizing colloid with the dispersed particle evidently occurs and the protective colloid acts as a solution link between the dispersed particle and the dispersion medium. The technology of producing a colloidal dispersion of a solid resin or plastic in water consists of breaking the solid mass into fine particles in the presence of water and a protective colloid. When the solid aggregates become sufficiently small, the protective colloid prevents coalescence. The amount of protective colloid used is generally 2–5% of the weight of the solid used. The breaking down or mastication of the solid can be done by grinding in a mortar and pestle or it can be accomplished in a ball mill, in which the shearing action of many pebbles or balls rotating in a closed container provides ample disintegration. A colloid mill may be used in place of a ball mill. In this case, a high shearing force is provided by the rotation of smooth discs set close to each other. In many cases it is advantageous to pre-soften the plastic with heat in order to facilitate the disintegration. When this is done, the process actually consists of dispersing a liquid in a liquid, as described below for emulsions. However, when such an emulsion is cooled, it consists of a colloidal dispersion of the solid plastic. Once the colloidal solution has been formed, it can be diluted to any desired concentration.

When a system is composed of tiny droplets of one liquid dispersed in a continuous phase of another liquid it is termed an *emulsion*. In plastics technology, this type of dispersed system is used in both the synthesis of polymers (page 34) and in the application of the finished product to such diverse uses as coatings, impregnations, adhesives and waterproofing. The preparation of an emulsion consists in most cases, of mechanically dispersing one liquid in another while preventing the coalescence of the droplets by the presence of

an emulsifying agent. If the material is a liquid such as the common plasticizers, or moisture-resistant oils, the emulsification may be carried out directly, but if it is a solid resin, the resin may be dissolved in a suitable solvent and this solution may in turn be emulsified.

The mechanical means of disintegration may vary from the simplest methods of rapid agitation by shaking or stirring, to more specialized types of equipment, such as colloid mills or homogenizers. In the latter case, the disintegration is effected by impinging the liquids against a solid barrier. The emulsifying agents used to produce the emulsion may be one of three types: crystalloid, colloid, or insoluble solid. The first group includes water-soluble salts of carboxylic, sulfonic, sulfinic, or phenolic acids. In the colloid class, the more common agents are ordinary soaps, proteins (casein, gelatin, glue), resins, starches, dextrans, triethanolamine soaps, and water soluble gums (e.g., gum arabic). The insoluble solid classification is less often encountered, but emulsions may be produced by the use of such solids as clay, calcium carbonate, basic ferrous sulfate, or copper sulfate. For such agents to be effective they must be finely subdivided. The soluble emulsifying agents cause a lowering of the surface tension of the continuous phase of the emulsion, while the insoluble emulsifying agents surround the tiny particles of dispersed material. In either case, the tendency of the separate particles to coalesce is prevented.



R_1C-CR = Emulsifying agent

CR_1 = Polar group (soluble in water) -amine or alkaline base such as ethylene diamine, morpholine, or ammonia.

CR = Nonpolar group (soluble in oil)—long chain fatty acids such as linseed, oleic, etc.

FIG. 13.13. (Courtesy of Bakelite Corporation.)

When two liquids are emulsified together one of two types of emulsions may be produced. These are known, respectively, as the "oil-in-water" and the "water-in-oil" types. The term oil in this case may refer to any liquid, usually of an organic nature, which is insoluble in water. Water is generally one of the components of an emulsion because of the reduction in cost thus effected. In an oil-in-water emulsion, the oil constitutes the dispersed phase and the water forms the continuous medium. In a water-in-oil emulsion the opposite is true. The water in this case is the discontinuous phase and the oil is the continuous phase. These two types of emulsions are diagrammatically illustrated in Figure 13.13. The type of emulsion which may be produced in each case depends upon the solubility of the emulsifying agent, the chemical nature of the phases involved, the ratio of volumes of these liquids, and the methods of mixing and agitation.

When successfully applied, emulsions or dispersions offer the following advantages ⁵:

1. High solids content at low viscosities.
2. Low solids content at high viscosities.

Either of the above results may be produced by regulations of phase relationships and emulsification conditions.

3. Controlled penetrations on porous surfaces.
4. Safety.
5. Economy.

To offset these factors, however, the following disadvantages often interfere with successful application of emulsion methods:

1. Poor water resistance of film.
2. Lowered speed of drying.
3. Excessive shrinkage.
4. Contamination of polymer with emulsifying agent.

Typical applications include coatings, adhesives, impregnation of fabric or paper, textile finishing or printing, and mold manufacture.

⁵ "Theory, Practice, and Uses of Resin and Lacquer Emulsions," American Resinous Products Corporation, Peabody, Mass., 1941.

Review Questions

1. What type of polymerization is involved in the case of acrylates? Indicate the reaction, using butyl methacrylate as the monomer.

2. Illustrate by means of outline reactions how acrylic esters and substituted acrylic esters may be produced.

3. What techniques are suitable for the polymerization of acrylic resins? Summarize each.

4. What effect does each of the following have upon the properties of the plastic prepared by solution polymerization:

- (a) temperature
- (b) concentration
- (c) concentration of catalyst
- (d) type of solvent
- (e) type of monomer?

5. How do the properties of the polymer produced vary with the nature of the monomer used?

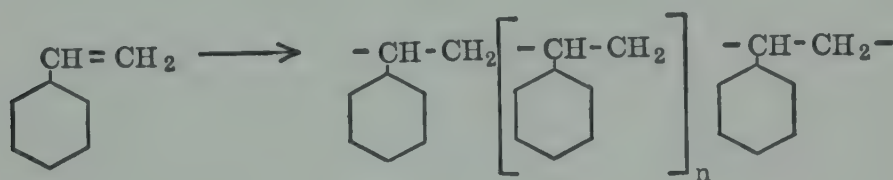
6. Explain the statement: "the methyl methacrylate polymer is capable of piping light."

7. What advantageous properties are exhibited by polymethyl methacrylate?

CHAPTER XIV

SYNTHETIC PLASTICS V: POLYSTYRENE

Polystyrene plastics, like the acrylate resins, are made from a monomer which contains the vinyl radical and hence may be considered as vinyl resins. The monomer, in this case, is styrene (vinylbenzene), and polymerizes according to the following equation:



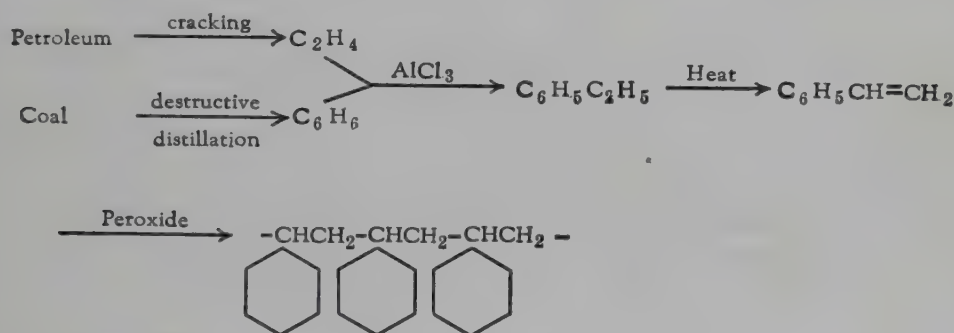
The history of the polymerization of styrene dates back to 1839. In this year, Simon found that heat and sunlight caused the conversion of styrene to a glass-like resin. In 1869, Bertholet found that the monomer could be obtained easily by the pyrolysis of ethylbenzene. At that time, the industrial possibilities were pointed out and its advantages, particularly for certain types of insulation, were considered. The awakened interest did not account for any far-reaching results, however, until in 1933, the Dow Chemical Company and the Du Pont Company independently started extensive investigations looking toward the commercial development of polystyrenes. Improvements in the methods of producing styrene and in controlling the polymerization were important factors leading to large scale production about 1937.

Manufacture and Polymerization of Styrene.—One of the difficulties encountered in the earlier pyrolyses of ethylbenzene was the formation of tarry by-products. This difficulty was overcome by passing the vapor of ethylbenzene and highly superheated steam into a tubular iron reactor to form a mixture having a temperature between 800 and 950° C. The mixture goes through the reactor at such a rate that it is above 700° C. for less than half a second. The yield of styrene is about 33%, based on the amount of ethylbenzene passed through the reactor or 67% based on the amount of ethylbenzene consumed during the reaction. No carbon or tar is formed in this procedure.

Another similar procedure is to pass a mixture of ethylbenzene and superheated steam over a dehydrogenation catalyst such as calcium oxide, alumina or silica gel at a temperature of about 650° C.

In addition to the pyrolysis of ethylbenzene as a source of styrene, it can be obtained as a by-product of the pyrolysis of propane at 800° C. It has been estimated that a plant capable of dealing with 5,000,000 cubic feet of propane per day could produce 59,000 liters of crude benzene which would contain 3400 liters of styrene.

The raw materials used for the commercial production of ethylbenzene are petroleum and soft coal. Ethylene is obtained from the cracking of certain petroleum fractions and benzene is obtained by the destructive distillation of soft coal. Benzene can also be obtained by the catalytic cyclization of *n*-hexane (from petroleum) and dehydrogenation of the cyclohexane formed. Benzene and ethylene combine in the presence of anhydrous aluminum chloride to form ethylbenzene. The following scheme represents the preparation of polystyrene from petroleum and coal:



The chemistry of the reaction by which polystyrene is produced is, in many respects, comparable to that involved in the polymerization of the acrylates. Like the latter, the methods of preparation may be varied according to the characteristics desired or the technique favored. Mass, solution and emulsion polymerizations are all applicable. The extensive study of all possibilities has resulted in the discovery of many limiting factors.

Most of the early work was concerned with investigation of the reaction catalyzed by heat and light. Later, experiments were carried out on the polymerization of emulsified styrene at low temperatures and also on the high-temperature polymerization of gaseous styrene. Meanwhile, the results of the investigations on liquid phase reactions were correlated so as to include the polymerization of styrene alone and polymerizations in solvents such as toluene, xylene, dioxan, chlorobenzene and carbon tetrachloride.

The more important conclusions ¹ will be stated briefly:

1. Polymerization occurs after an induction period. This activation time may vary from several minutes to several days.

2. The activation of the double bond is due to the higher state of energy induced by the action of heat and light. The time required and the final energy level reached are dependent upon reaction conditions.

(3) It is generally agreed that the activated form may be represented as a highly energized molecule ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$) or as a biradical ($\text{C}_6\text{H}_5\text{CH}-\text{CH}_2$).

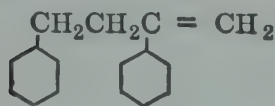
(4) The second step of the reaction may be considered as the growth process. The polymer chain may grow in one direction in the case of activated monomers or in two directions when a biradical type is involved. This reaction is exothermic and rapid.

(5) Termination of the chain involves many possible chain-breaking mechanisms similar to those previously outlined. (See p. 48.)

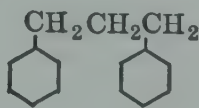
(6) A high degree of branching may occur according to the conditions used. This is due to the introduction of an extra free bond along the chain. (See p. 40.) Traces of divinylbenzene cause cross-linking.

(7) The exact configuration of the polymer is still open to debate. Some investigators such as Staudinger and Steinhofer ² support a "head-to-tail" arrangement, $-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-$. These inves-

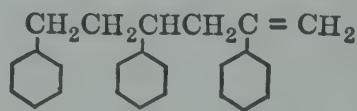
tigators found that the pyrolysis of polystyrene yielded styrene, "distyrene" (I), 1,3-diphenylpropane (II) and "tristyrene" (III).



(I)



(II)



(III)

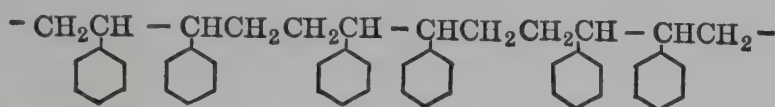
These pyrolysis products indicate the existence of a 1,3 or "head-to-tail" arrangement. On the other hand, Midgley, Henne and Leicester ³ obtained 1,4-diphenylbutane, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, by

¹ Mark and Raff, *High Polymeric Reactions*, pp. 325-344, Interscience Publishers, Inc., New York (1941).

² Staudinger and Steinhofer, *Ann.* **517**, 35 (1935).

³ Midgley, Henne and Leicester, *J. Am. Chem. Soc.* **58**, 1961 (1936).

treating styrene with sodium and alcohol. They interpret their results on the assumption that a dimer of styrene is formed and is then reduced. On the basis of this evidence, they favor a "head-to-head, tail-to-tail" structure for polystyrene, e.g.,



(8) In the absence of any material catalyst, light was found to be essential for the reaction to proceed at a measurable rate. The percentage which was polymerized per unit of time was independent of the length of the irradiation. The rate of polymerization was increased if oxygen from the air was also available.

(9) Stobbe and Posnjak⁴ in a series of trials found that freshly-distilled styrene polymerized much more slowly than monomeric material that was distilled fourteen days before polymerization. The formation of "polymerization nuclei" in the aged purified sample was postulated.

Emulsion Polymerization.—Emulsion polymerization proceeds rapidly even at low temperatures. It is interesting to note that the average molecular weight of the polymer molecules obtained by emulsion polymerization is usually greater than that obtained by mass polymerization. This is illustrated by the data obtained by Staudinger and Husemann⁵ and given in Table I-14.

TABLE I-14.

Temperature of Polymerization	Mol. Wt. in Emulsion	Mol. Wt. in Mass Reaction
30°	750,000	600,000
60°	400,000 275,000	350,000
100°	175,000	120,000

Gaseous Polymerization.—Breitenbach⁶ found that measurable polymerization of gaseous styrene proceeds at elevated temperatures

⁴ Stobbe and Posnjak, *Ann.* **371**, 259 (1910).

⁵ Staudinger and Husemann, *Ber.* **68**, 1691 (1935).

⁶ Breitenbach, *Oester. Chem. Ztg.* **11**, 232 (1939).

to form low molecular weight polymers. The higher the temperature used, the lower the molecular weight of the polymers.

Effect of Miscellaneous Agents.—Numerous investigators have sought to determine the effect of various agents on the polymerization of styrene. The active materials may be divided into three distinct groups:

1. *Catalysts.* Organic peroxides, e.g., benzoyl peroxide, hydrogen peroxide and oxygen increase the rate of polymerization and lower the molecular weights of the products.

2. *Inhibitors.* Hydroquinone is one of the most effective and most widely used inhibitors. This class of compounds causes a more or less extended induction period and hence lowers the over-all rate of polymerization. In many cases, the inhibitor will prevent any polymerization for months or years. To cause the polymerization of an inhibited monomer containing hydroquinone, a sufficient amount of peroxide is added to oxidize the inhibitor and to catalyze the polymerization.

3. *Retardants.* These substances cause the reaction to proceed at a slower rate and hence raise the molecular weights of the polymers obtained. Aromatic nitro or phenolic compounds are examples of retardants.

By proper adjustment of the experimental conditions, it is possible to obtain polymers of widely varying molecular weights. Although polystyrene having a molecular weight of 1,000,000 has been prepared, the most useful products are found to have molecular weights in the region of 125,000. Polymers having still lower molecular weights, about 35,000, are finding increasing uses in the varnish industry.

Compounding and Fabrication.—In most applications, polystyrene plastics are used with no modifying agents except possibly pigments or dyes, and a small amount of lubricant. Since a wide range of softening points and flow characteristics is possible by modification of the polymerization procedure to produce polymers of varying molecular weights, plasticizers are rarely used. Another reason for avoiding the use of plasticizers is that desirable features such as electrical resistance and low moisture absorption may be unfavorably affected by their inclusion. Compounding of polystyrene base plastics is, therefore, generally very simple. Because of the desirable transparency of polystyrene, fillers are rarely used.

Polystyrene can be processed by the customary methods used for plastics. Of particular interest is the steadily increasing use of this plastic in injection molding. The broad temperature range

in which polystyrene polymers of different molecular weights may be used, and the valuable combinations of properties which can be produced are responsible for its popularity in this molding method. Some of the largest injection-molded products may be prepared from polystyrene because of its favorable flow characteristics. Associated with this fabrication method, of course, is the use of the basic plastic in extrusions. Pre-fabricated forms of sheets, rods, and tubes are used in large quantities. The absence of plasticizers permits relatively higher temperature resistance in a variety of products. Very little shrinkage occurs during the molding process. This feature simplifies the work of the molder, for shrinkage of the resin during molding is an important problem to be solved by the molder in the regulation of tolerances in dimensions.

Compression molding is rarely used with polystyrene because the costs are greater and the processing is more difficult than in the case of injection molding. The monomer or partially polymerized resin, however, can be cast by heating the prepared forms for three to five days at about 130° C. The time factor is generally undesirable for production efficiency. Cast samples of sheet or foil-like nature may be formed from solutions. The most effective solvents for polystyrene are aromatic hydrocarbons, chlorinated hydrocarbons and esters.

Finally, the use of polystyrene in adhesives and coatings must be mentioned. The adhesive character is enhanced by incorporation of Arochlor resins (chlorinated biphenyl) and coumarone-indene resins. Such resins and also cellulose esters may be compounded with polystyrene in the manufacture of coatings. The coating consists of polystyrene (molecular weight about 35,000) and the resin or cellulose ester, dissolved in a suitable solvent, such as chlorinated or aromatic hydrocarbons and to a limited extent, esters. These relatively low molecular weight polystyrenes are soluble in drying oils such as tung oil and hence can be used in the making of varnishes. High molecular weight polymers can be used as coatings if first plasticized with tricresyl phosphate, dibutyl phthalate or other suitable plasticizer.

In summary, the fabrication of polystyrene is not difficult. The raw material is supplied in a variety of forms—molding powders, emulsions, solutions, pre-fabricated shapes—and many avenues are open to a processor. Difficulties such as softening from frictional heat and creation of internal stresses are often encountered, however, in the finishing and machining of the plastic. Mold design and construction should simplify such problems to as great an extent as possible.

Properties and Applications.—Since polystyrene is a thermoplastic polymer, it is subject to most of the restrictions of this family. However, polystyrene approaches the ideal plastic in its physical properties more closely than any other industrial type at the present time. The heat resistance, as in the case of other thermoplastics, is low. The average maximum temperature at which the molded polystyrenes retain their strength is in the vicinity of 75°C . The top operating temperature often goes as high as $90\text{--}95^{\circ}\text{C}$. In common with other thermoplastics, the heat resistance is improved as the average molecular weight of the polymer increases. With an increase in the molecular weight, however, there is a decrease in the ease of fabrication. Incorporation of a plasticizer will facilitate fabrication operations, but will cause a decrease in heat resistance. At low temperatures, it has been found that polystyrene is particularly valuable. The strength and impact resistance are retained to a remarkable degree even in contact with dry ice. The impact resistance of polystyrene which has been cooled with dry ice is 0.275 foot-pounds. Such a property is of great importance in the use of this plastic for aircraft applications. The variations of tensile strength and elongation of injection-molded polystyrene with changes of temperature are shown in Figures 14.1 and 14.2.

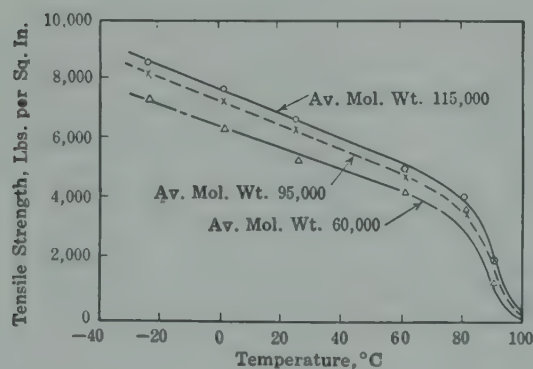


FIG. 14.1.

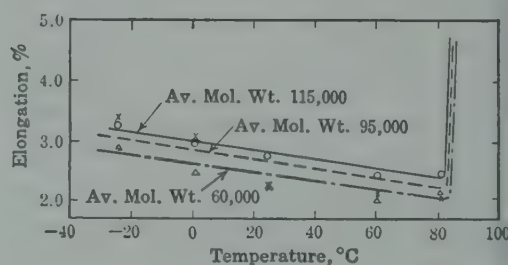


FIG. 14.2.

FIGS. 14.1, 14.2. Effect of temperature upon tensile strength and elongation of polystyrene of various molecular weights. (Carswell, Hayes and Nason, *Ind. Eng. Chem.*, **34**, 456, 1942.) (Courtesy of Monsanto Chemical Company.)

The impact resistance under ordinary conditions is not generally as high as that exhibited by many other types of plastics, as shown in Table II-14. The flexural and tensile strengths are comparable to those of other types. Products which are subject to constant flexing or bending may develop tiny surface cracks over a long period of

time. This effect is known as "crazing." Polystyrene also possesses good elasticity at temperatures up to 75–80° C.

TABLE II-14. IMPACT RESISTANCE, MEASURED IN FOOT-LBS.^a

Polystyrene	0.35–0.50
Ethyl cellulose	0.6 –1.8
Cellulose nitrate	2.0 –8.0
Cellulose acetate	0.7 –4.2
Polyvinylidene chloride	1.0 –4.0
Polyacrylate	0.25–0.50
Ureas	0.28–0.32

^a A Ready Reference for Plastics, p. 55, Boonton Molding Company, Boonton, N. J., 1943.

Polystyrene resin is noted for its excellent electrical characteristics, extremely low moisture absorption, and favorable dimensional stability. It shares, with polyethylene, the distinction of having much better electrical properties than any other plastic known at the present time. The extremely low power factor (0.0001–0.0004) combined with its high dielectric quality are responsible for its widespread use as an insulating medium. The fact that its low loss factor is exhibited at high frequencies has placed polystyrene in a class equivalent to fused quartz as a dielectric. This property has been and will continue to be of great importance in the further development of both radio and television.

Combined with the usefulness of the electrical properties under ordinary conditions is the fact that these characteristics are retained under a wide range of humidity or moisture conditions. The water absorption after 24 hours immersion is recorded as 0.00% while 318 hours of immersion causes the absorption of only 0.05% of water. This exceptional resistance to moisture accounts, in part, for the high dimensional stability exhibited by the plastic. This factor permits the molding and retention of shape of complicated molded products. The absence of plasticizer also aids the retention of intricate designs.

The polystyrene plastics are similar to the acrylates, and are often directly compared with them, because of the excellent light transmission and favorable refractive index of the plastic. The transparency, beauty, and wide range of suitable colors are responsible for many of the applications of polystyrene. The combination of light transmission, excellent electrical characteristics and moisture resistance is particularly favorable. The light transmission of this

plastic (87–91%) is not quite as high as that of polymethyl methacrylate (92–93%) but it compares favorably with that of the best plate glass (85–87%).

Varnishes prepared from relatively low molecular weight polystyrene and drying oils combine excellent flexibility and film strength with high resistance to moisture. This combination of properties is



FIG. 14.3. (Courtesy of The Dow Chemical Company.)

seldom found in resin-oil varnishes, and is valuable in the manufacture of waterproof sandpaper, varnished tapes for electrical insulation, coatings for metal food containers and improving the moisture resistance of films used for packaging foods. A mixture of 50% polystyrene and 50% drying oil is generally used. A higher proportion of drying oil provides a more flexible film, but it has decreased resistance to moisture.

Various miscellaneous properties exhibited by polystyrene but not associated with this plastic alone may also be mentioned. The low specific gravity, for example, is a desirable characteristic in many applications. Further, it permits a greater volume production per pound of base resin. Then, too, exceptionally high general chemical resistance is exhibited by polystyrene. This includes good resistance to more or less concentrated oxidizing acids, organic acids, salt water, alkalies, animal and vegetable oils, and alcohols. Other general characteristics of low flammability, odorlessness and tastelessness are also favorable.

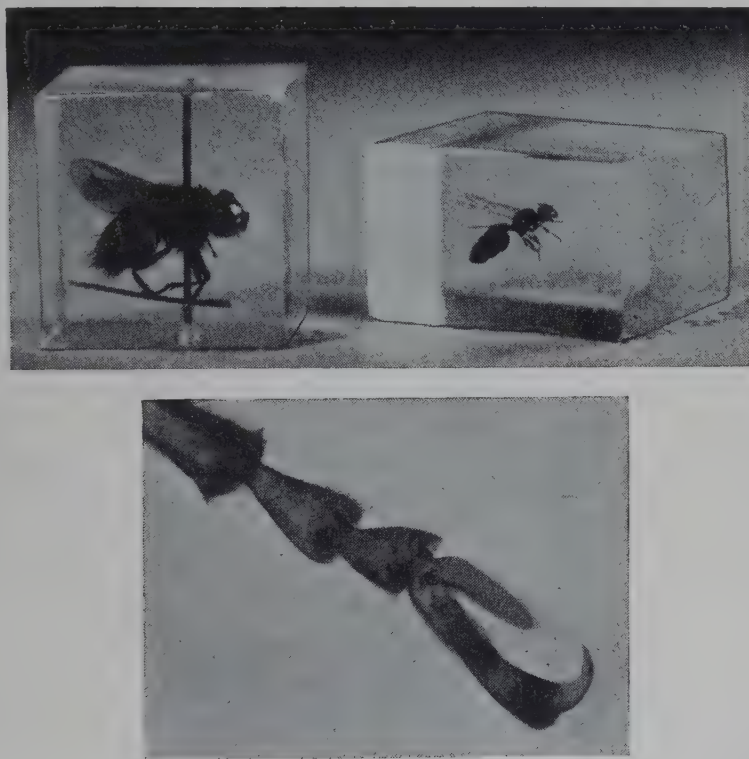


FIG. 14.4. The remarkable properties of clear, transparent polystyrene make it an excellent medium for the preservation of natural history specimens. (Courtesy of The Dow Chemical Company.)

Polystyrene is used in making such articles as battery containers (Figure 14.5), refrigerator parts, radio insulation, toilet articles, medical equipment, kitchen utensils, coatings, wire coverings, acid containers, decorative mechanical parts, packaging foil, and lighting fixtures.

The product is sold under the trade names Loalin, Lustron, Piccolastic, Styron, and Bakelite Polystyrene. A polydichlorostyrene

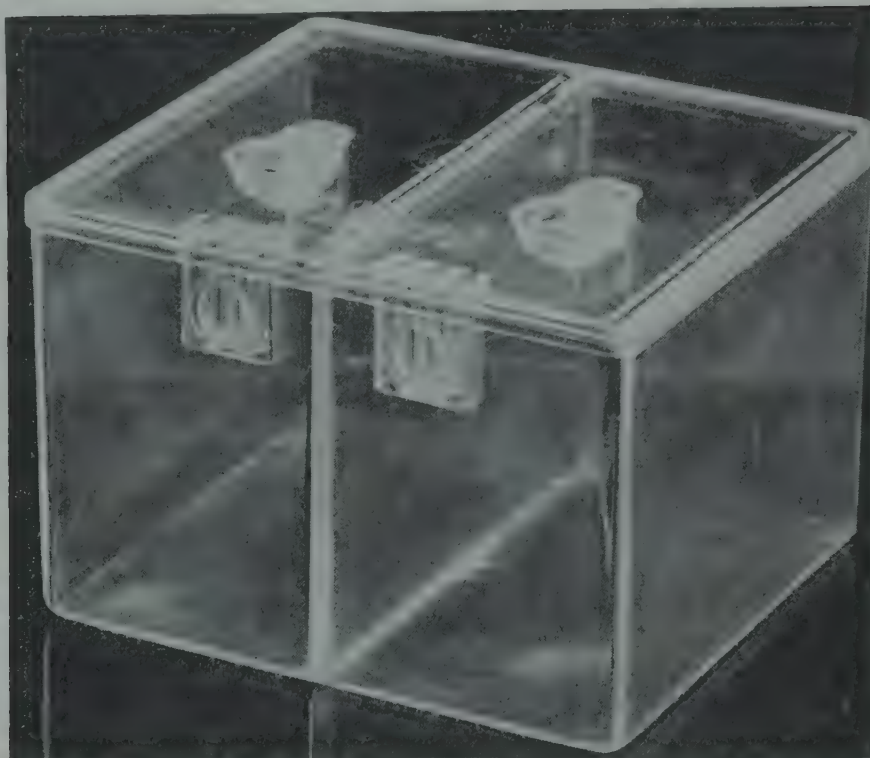


FIG. 14.5. Battery case made from polystyrene.
(Courtesy of Monsanto Chemical Company.)

known as Styramic HT has been developed, which possesses better heat resistance than polystyrene while retaining the excellent electrical characteristics of polystyrene.

Review Questions

1. What methods are used for the production of styrene? Include equations for the reactions involved.
2. Discuss briefly:
 - (a) Branching in the styrene polymer
 - (b) Effect of divinylbenzene in the reaction mixture
 - (c) Configuration of the polymer
 - (d) Catalysis by light
 - (e) Effect of polymerization method upon molecular weight of polymer.
3. Why are plasticizers omitted in the compounding of polystyrene?
4. What are the two principal advantages of polystyrene?
5. Compare the properties of polystyrene with those of polymethyl methacrylate.
6. Select five advantageous properties of polystyrene and illustrate their importance by examples of specific applications.

CHAPTER XV

SYNTHETIC PLASTICS VI: VINYL FAMILY

Although such plastics as the acrylates and polystyrene are correctly classified as vinyl derivatives ($\text{CH}_2=\text{CHX}$), the term, as generally used in industry, refers to those plastics which are specifically named *polyvinyl*. Thus, the group includes the following well-known and widely used products:

polyvinyl acetate
polyvinyl chloride
polyvinyl chloride-acetate copolymer
polyvinyl alcohol
polyvinyl acetals
polyvinylidene chloride.

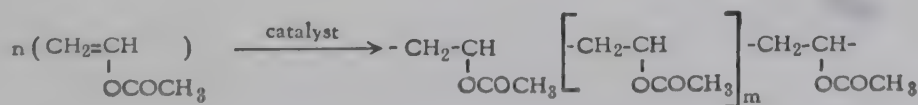
The family includes several types which differ from each other only in the nature of the atom or group which is linked to the vinyl radical. The list of derivatives which are of importance in this family is constantly growing. New types such as vinyl ketones and vinyl ethers are coming into prominence, and modifications are being made in the chemical structure of the older types.

As a class, the vinyl polymers have risen rapidly to a position of major importance in the plastics world. Because of the great variability of fundamental properties and, therefore, range of applications, these plastics occupy an enviable position. Being thermoplastic, the possible uses are restricted to some extent. However, they are used extensively in such diversified fields as coatings, adhesives, extrusions, moldings, and pre-fabricated stocks.

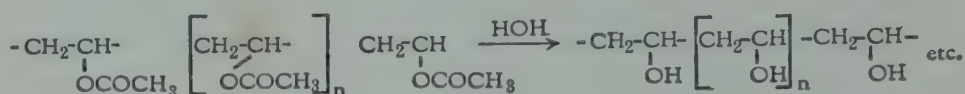
There are two general methods of preparing vinyl polymers:

1. Addition polymerization of the monomer involved.
2. Chemical conversion of the substituent groups of a polymer.

The first method may be represented by the polymerization of vinyl acetate:



The second method involves the conversion of the acetate substituent group to another group by a simple reaction such as hydrolysis.



This reaction need not be carried to completion and a large number of products, having varying proportions of hydroxyl and acetate groups, may be obtained. Some of these will be discussed later under the heading, Polyvinyl Alcohol.

Polymerization methods are very similar to those described for polystyrene. The reaction proceeds most satisfactorily in solution or in an emulsion under the influence of peroxides, heat, and light. Mass polymerization can be carried out, but it is more difficult to control. It has been found that iron, zinc, nickel, copper and minute quantities of iron salts exert an inhibitory effect on the polymerization of vinyl compounds and tend to cause the formation of brittle resins which are not very stable toward heat. The equipment used for these polymerizations is preferably lined with lead. A nickel-chromium alloy steel container has proved satisfactory, and glass-lined reaction vessels can be used. The exact configuration of the polymer (i.e., molecular weight distribution, degree of branching, etc.) depends upon the conditions used in the preparation. Concentration, nature and amount of catalyst used, temperature and pressure, and ratio of monomers when copolymerization is used, are all effective in determining the structure of the polymer and consequently its properties.

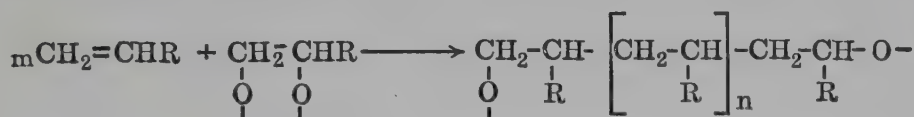
POLYVINYL ACETATE

Manufacture.—The monomeric vinyl acetate is produced by the addition of acetic acid to acetylene. This reaction is carried out by passing acetylene through a suspension of finely divided mercuric sulfate in acetic acid. The reaction temperature is kept at about 35° C., and acetylene is passed through the suspension at such a rapid rate that most of the vinyl acetate (b.p. 73° C.) formed is carried out of the suspension in the excess acetylene gas. By proper control of temperature, catalyst and circulation rate, yields of 80% of vinyl acetate are obtained. At higher temperatures, above 70° C., ethylidene diacetate is the chief product of the reaction.

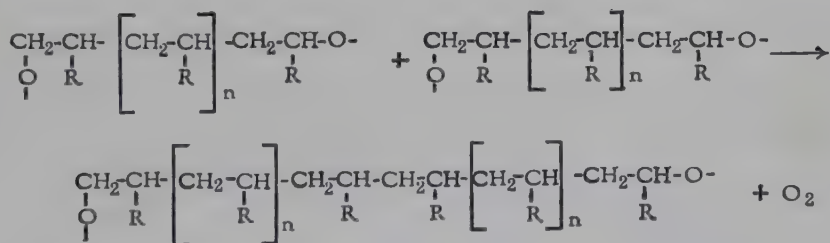
Polymerization of the vinyl acetate may be accomplished with the undiluted monomer, or in the form of a solution or an emulsion. Growth is believed to occur by means of a chain reaction and can

be followed by the ordinary methods of physical measurements such as index of refraction or dilatometric observations. Acceleration of the conversion is caused by use of a catalyst such as ozone, hydrogen peroxide, benzoyl peroxide, acetyl benzoyl peroxide and tetraethyl lead. As might be expected, the rate of polymerization is dependent upon the amount of catalyst used.

The roles played by the added peroxide, by oxygen of the air and by peroxide impurities present in ordinary vinyl acetate have been the subject of considerable investigation. The fact that pure vinyl acetate does not polymerize to any appreciable extent at 100° even when in contact with oxygen indicates that the reaction is dependent upon the presence of some peroxide in the monomer. Actually, commercial samples of vinyl acetate have been found to contain small amounts of peroxide. Further, the fact that the quantity of peroxide found in the monomer is increased by irradiation with ultra-violet light, explains the role of sunlight or other source of ultra-violet light in hastening polymerization. The absorption of oxygen during the irradiation is accomplished by an inhibiting period, particularly at temperatures below 120° C. After this inhibiting period, however, the reaction may proceed in an atmosphere of either nitrogen or oxygen, with the liberation of oxygen. These facts are explained by the following mechanism of polymerization.



The liberation of oxygen is explained as resulting from the union of two chains, as shown below:



The course of the polymerization in solution and emulsion form indicates that the generalizations which apply to mass reactions may be extended to these. In solution polymerizations, the reactions may be modified by exchanges between the growing radicals and the solvent molecules. The effect varies with the type of solvent, the temperature, concentration, and amount of catalyst. For example,

the polymer obtained by the polymerization of vinyl acetate in chloroform contains chlorine. In emulsion polymerizations the possibility of hydrolysis of the polymer must be avoided by careful regulation of the pH value of the emulsion. The use of alkaline emulsifying agents can be avoided by using a 5% aqueous solution of polyvinyl alcohol as the emulsifying agent. With this emulsifying agent, polymerization can be accomplished with 0.1% of hydrogen peroxide and 0.3% of formic acid, both percentages being based on the amount of vinyl acetate used.

Photopolymerization and polymerization under pressure have received some attention. It is interesting to note that in the latter case, oxygen, surprisingly, had no effect while hydroquinone, a normal inhibitor, actually increased the rate of polymerization.

Polymerization of vinyl acetate may be stopped by the action of certain inhibitors. An example of such action is the fact that the addition of 1% of sulfur completely inhibits polymer growth.

Compounding and Fabrication.—The properties of polyvinyl acetate are best enhanced by suitable compounding technique. Chief among the compounding agents generally applicable is a broad field of plasticizing agents. Numerous high-boiling organic liquids—particularly those of the ester type—serve to flexibilize and increase the toughness of the plastic product. Typical plasticizers are dibutyl and diamyl phthalate, triphenyl phosphate and triglycol di-(2-ethyl hexanoate). The particular plasticizer to be used is selected on the basis of the properties desired in the final product. Furthermore, since polyvinyl acetate is available in a variety of molecular weights, the amount and nature of the plasticizer used will depend upon the molecular weight of the base resin.

Various dyes, pigments, lubricants, solvents or modifying resins may be used in conjunction with the plasticized polyvinyl acetate. Such resins as gum dammar, rosin, nitrocellulose, chlorinated rubber, some glycerol-phthalate and some phenol-formaldehyde resins may be added to produce plastics having varying properties. When polyvinyl acetate is used as a molding compound, a high proportion of filler is incorporated. If too high a proportion of filler is used, a decrease in tensile strength, elongation and impact resistance may be expected. Molding technique involves the use of special alloy molds, pressures of 1500–2000 lbs. per sq. in., and temperatures of 107–120° C. Cooling to 32° C., is recommended before removal. Because of the difficulties of low softening point (45–90° C.) and excessive sticking to the mold, the scope of this application is limited.

The most important applications of polyvinyl acetate result from the use of solutions or emulsions. These resins are generally soluble in ketones, esters, chlorinated hydrocarbons, nitroparaffins, aromatic hydrocarbons and methanol. Polyvinyl acetate is insoluble in other anhydrous alcohols and in water. It is surprising, therefore, to find that polyvinyl acetate is soluble in 95% ethyl alcohol and in other low-boiling alcohols (e.g., isopropyl and *n*-butyl alcohols) which contain about 10% of water. The solvents most frequently used are acetone, methyl acetate, toluene and methanol. The amount of solid dissolved in the commercially available solutions varies from 24% to 70%.

Emulsions are made by first dissolving the polyvinyl acetate and plasticizer in an organic solvent which does not mix with water and adding this solution, with vigorous stirring, to water which contains a suitable emulsifying agent. The emulsion is then passed through an homogenizer or colloid mill in order to increase its stability. A small amount of bentonite may be added to the finished emulsion to act as a protective colloid. This treatment increases the stability of the emulsion when it is to be stored for some time. A more feasible method of forming a plasticized polyvinyl acetate emulsion is by the emulsification of monomeric vinyl acetate followed by polymerization of this form. Unreacted monomer may be separated by steam distillation or by blowing with hot air, and the adjustment of plasticizer content may be made by adding emulsified plasticizer to the dispersed resin. A typical plasticizer emulsion may contain:

- 1.9 liters plasticizer (dibutyl phthalate)
- 1.8 liters water
- 28.35 grams triethanolamine
- 56.7 grams oleic acid.

In the production of this emulsion, the oleic acid is mixed with the plasticizer, and this mixture is added, with rapid stirring, to the triethanolamine-water mixture.

Solid polyvinyl acetate is marketed in several different grades having different molecular weights. It is also available in solutions, emulsions, molding compositions and pre-fabricated sheets. The trade names are "Vinylite A" series (solids), "Vinylseal" (solutions), "Gelva" (solid) and "RH" (available in solid, emulsion or solution form). The differences in the molecular weights of the various grades are represented by the softening points of the "Vinylite A" series, given in Table I-15.

TABLE I-15. SOFTENING POINTS OF "VINYLITE" POLYVINYL ACETATE RESINS^a

Resin	Softening Point, ^b °C.
AYAB	44.0
AYAA	66.0
AYAF	77.0
AYAT	86.5
AYAW	88.5

^a "Vinylite" Polyvinyl Acetate Resins, Carbide and Carbon Chemicals Corporation, New York, 1942.

^b Approximate values determined by modified ball and ring method.

The viscosities, expressed in centipoises, of molar solutions of RH-polyvinyl acetate in benzene are shown in Table II-15. Table III-15 gives the different concentrations of solutions of several polyvinyl acetates which have the same viscosity.

TABLE II-15. VISCOSITIES OF RH-POLYVINYL ACETATE^a

Resin	Viscosity
RH-838	650-1000
RH-837	80-115
RH-836	15-20
RH-411 ^b	4-6

^a R and H Technical Bulletin No. 4-243, E. I. DuPont de Nemours and Co.

^b Methanol was the solvent used for RH-411. All viscosities measured with a Hoeppler viscosimeter.

TABLE III-15. CONCENTRATION OF POLYVINYL ACETATE SOLUTIONS^a

Relative Concentration By Weight of "Vinylite" Polyvinyl Acetate Solutions at a Constant Viscosity of 250 Centipoises at 20° C.

Solvent	Resins				
	AYAB	AYAA	AYAF	AYAT	AYAW
Acetone	53%	39%	31%	26%	17%
Toluene	47%	32%	26%	22%	14%
Butyl Acetate	45%	31%	25%	21%	13%

^a Courtesy Carbide and Carbon Chemicals Corporation.

Properties and Applications.—Polyvinyl acetate is a colorless, odorless, tasteless substance which burns only slowly. Its principal use is in the forming of films and adhesives. The films may be modified with plasticizers to give almost any degree of flexibility. These films are tough, have good tensile strength and are resistant to water, dilute acids, salts, mineral and vegetable oils. They are not affected by oxidation or aging. The film strength, toughness, softening temperature and viscosity in solution all increase with increasing molecular weight of the polymer.

The films may be deposited from either solutions or emulsions by means of any of the usual methods, such as dipping, roll-coating, knife-coating, brushing or spraying. The films usually obtained are transparent. Solutions of low molecular weight polymers are used for spraying purposes because solutions of high molecular weight polymers, when sprayed, tend to "string" badly. However, emulsions of high molecular weight polymers can be used without "stringing." Since polyvinyl acetate films tend to retain a small amount of solvent for a long period of time at room temperature, they are usually dried by heating to 110–120° C., for a few minutes. These films are used to coat surfaces of wood, cloth, paper, metals, tile, concrete and ceramic bodies. An important commercial use is as a lining or coating for food containers. Polyvinyl acetate films are used to impart strength, water resistance, grease resistance and transparency to paper used for wrapping food.

The most important use of polyvinyl acetate is as an adhesive. It has proved to be very satisfactory for the bonding of such widely different substances as cellophane, cloth, paper, cardboard, plastic films, cork, wood, leather, glass, mica, stone, porcelain and metal. These adhesive solutions may be used either at room temperature or with the application of heat. When a cold adhesion is to be made, the two surfaces to be bonded are coated with a solution of polyvinyl acetate and allowed to stand until the solvent has evaporated sufficiently to cause the film to become tacky. The two surfaces are then pressed firmly together and held under pressure until all of the solvent has evaporated. This method is applicable only when the substances to be bonded have porous surfaces. A good bonding may be obtained more quickly if it is possible to heat the plastic until it softens or becomes tacky. In this procedure, the polyvinyl acetate may be applied to the surfaces in either solution or emulsion form and heated until the solvent has evaporated completely and the plastic has become tacky. The tacky surfaces are then pressed together and allowed to cool. It is also possible to use a solid plasticized

polyvinyl acetate composition as an adhesive in a hot-melt application. The ultimate strength of the bond is reached immediately upon cooling. This procedure can be used with surfaces which are relatively non-porous.

Representative formulas of adhesives are

(1) Polyvinyl acetate (high viscosity)	100 parts
Tricresyl phosphate	25 "
Toluene	300 "
Ethyl acetate	100 "
(2) Polyvinyl acetate (medium viscosity)	100 "
Arochlor 1260	15 "
Ester gum	15 "
Dibutyl phthalate	15 "
Ethyl acetate	200 "
Toluene	200 "

Polyvinyl acetate can be used as an adhesive in making plywood, for gluing parts of shoes together and as a binding tape adhesive. When mixed with wood flour and a suitable solvent, it forms "plastic wood." Aluminum foil may be bonded to paper with polyvinyl acetate. For special applications, e.g., joining leather to metal, a polyvinyl acetate emulsion containing 6–40% of rubber latex, is especially valuable. Polyvinyl acetate is used as a size and stiffening agent for textiles, and, when suitably plasticized, as a finishing agent for leather. Lacquer solutions of plasticized polyvinyl acetate are adaptable as vehicles for aluminum bronze paints.

POLYVINYL CHLORIDE

Polyvinyl chloride is a thermoplastic, linear macro-molecule produced by the addition polymerization of vinyl chloride, $\text{CH}_2=\text{CHCl}$. The observation that a polymer is formed by self-addition of such a molecule was made in 1838 by Regnault. Very little progress in the knowledge of the behavior of vinyl halides was made from that time until 1917. The preparation and polymerization of the three vinyl halides (chloride, bromide and iodide) was then studied, and the vinyl polymers began to receive attention from those who visualized the possibilities of a great future for them in the field of synthetic polymers.

Manufacture.—Vinyl chloride is a gas whose boiling point is -13.9°C . It can be prepared conveniently by passing a mixture of acetylene and hydrogen chloride over suitable catalysts, e.g., mercuric

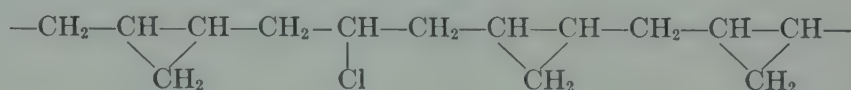
chloride on silica gel at 20–30° C., or activated charcoal at 200° C. It can also be obtained by passing a mixture of hydrogen chloride and acetylene through hydrochloric acid solutions of metal chlorides at 60–80° C. The polymerization of vinyl chloride is similar to that of vinyl acetate. The growth of the polymeric chain involves activation followed by self-reaction according to a chain mechanism. The polymerization may be brought about either in excess monomer or in an inert solvent such as ketones or alcohols. Effective catalysts include organic peroxides, tetraethyllead and ozone. On the other hand, hydroquinone is an excellent inhibitor of the polymerization. In the study of photopolymerizations, it was found that easy polymerization occurs only in the extreme ultra-violet, unless certain sensitizing agents are added. The addition of uranium salts, however, has been found to cause polymerization even in the region of visible light. The reaction kettle in all cases should be lined with the same materials that were recommended for the polymerization of vinyl acetate (p. 272).

Mass polymerization of vinyl chloride results in the formation of an insoluble polymer which precipitates from the excess monomer. In general, polymerization is more satisfactorily controlled in solution or in an emulsion. When polymerization is carried out in a solvent, the resulting polymeric molecules have widely different molecular weights. This is believed to be due to the decrease in concentration of the monomer as polymerization proceeds. By causing polymerization in a liquid which is a solvent for the monomer and a non-solvent for the polymer, it is possible to add monomer gradually to the solution at the same rate at which the polymer is precipitating. In this way, the concentration of the monomer is kept constant and by frequent removal of the polymer by filtration, the process is continuous. The molecular weights of polymers produced by this method are in a relatively narrow range. Also, it is found that the molecular weights produced in a mass polymerization lie within a narrow range. It is evident that once the monomer has been activated and starts to grow, it grows with extremely great rapidity to its ultimate length. In common with all other polymerizations of ethylenic compounds, higher temperatures increase the rate of polymerization, and cause the formation of products having relatively low molecular weights.

It has been found that the ease of polymerization of different vinyl halides varies in the order: vinyl iodide > vinyl bromide > vinyl chloride. Vinyl fluoride does not polymerize alone, but will co-polymerize with any of the other vinyl halides. Vinyl bromide

and vinyl iodide are, of course, much more expensive than vinyl chloride. Consequently no commercial uses have been found for polyvinyl bromide or polyvinyl iodide.

The structure of polyvinyl chloride has been studied by a number of investigators, but the most significant contributions to the structure of vinyl polymers have been made by Marvel and his co-workers.¹ The principal problem has been to determine whether the vinyl chloride units are linked together in a "head-to-tail" (1, 3) arrangement or a "head-to-head, tail-to-tail" (1, 2) arrangement. A reaction which would be of value in distinguishing between these two arrangements is the removal of halogen with zinc. It is well-known that zinc removes halogen atoms in the 1, 2-position forming olefinic linkages and also that zinc removes halogen atoms in the 1, 3-position forming cyclopropane derivatives. When a very dilute solution of polyvinyl chloride in dioxane is heated with zinc, 84–86% of the chlorine is removed. The product does not reduce potassium permanganate solution, a fact which indicates that cyclopropane rings are formed. The fact that only 84–86% of the chlorine is removed is explained on the basis of probability. If there are pairs of atoms which may react with a given reagent to form a new grouping, e.g., formation of a cyclopropane ring by removal of the two chlorine atoms with zinc, there is a chance that occasional atoms will become isolated, as indicated in the formula below:



The probable percentage of these isolated atoms has been calculated by Flory² who found that 13.53% of these atoms would be expected to be isolated, while 86.47% would be involved in the reaction. This figure of 86.47% compares very favorably with the 84–86% of chlorine actually removed by zinc. It should be mentioned that all of the halogen would be removed by treatment with zinc if the halogens were present in the 1,2-positions. Further evidence which supports the belief that the 1,3-arrangement is correct is that when polyvinyl chloride is warmed with potassium iodide solution, no iodine is liberated. A 1,2-dichloride would react with potassium iodide forming an olefinic linkage and liberating iodine.

There is some evidence to indicate that certain vinyl chloride

¹ For lead reference, see Marvel and Inskeep, *J. Am. Chem. Soc.* **65**, 1710 (1943).

² Flory, *J. Am. Chem. Soc.* **61**, 1518 (1939).

polymers have branched chains. Branching apparently occurs more frequently if the polymerization temperature is relatively high.

Compounding and Fabrication.—Polyvinyl chloride is always plasticized by the incorporation of a high proportion of plasticizer to decrease its inherent rigidity. The effectiveness of a plasticizer in the thermoplastic field depends upon its solvation of the base resin. The greater insolubility of the chloride derivative as compared with polyvinyl acetate necessitates the use of a higher proportion of plasticizer. By the addition of sufficient plasticizer (added at an elevated temperature), the gel state is eventually produced and, in this condition, the plasticized resin may be poured when heated. For more general applications of molding, extrusion, and sheeting, the amount of plasticizer is dependent upon the heat resistance and flexibility desired. One of the most popular forms of the plasticized resin in the industry is known as "Koroseal" or "Geon."³ This product may be altered by varying the molecular weight of the polyvinyl chloride used and by varying the nature and amount of the plasticizer, in order to satisfy a range of requirements. Certain types may contain as high as 85% plasticizer. The most popular plasticizers for all-purpose application are tricresyl phosphate, dioctyl phthalate and dibutoxyethyl phthalate. Figure 15.1 shows the effect of the proportion of plasticizer on tensile strength, elongation and hardness of Geon compounds.

The plasticized products may be further compounded as described for polyvinyl acetate. Dyes, pigments, lubricants, diluent resins, and fillers may be added as required for the attainment of specified properties. By the use of different fillers, for example, the properties of hardness, strength, flexibility and elongation may be varied widely. The main divergence between the acetate and chloride types lies in the different methods used for their application. The acetate is of major interest in solution; the chloride is generally molded or extruded. Molding techniques require conditions of 1000–2000 lbs. per sq. in., at temperatures of 120–135° C. When polyvinyl chloride is molded at too high a temperature, it decomposes with charring and the liberation of hydrogen chloride. The addition of alkaline earth carbonates, hydroxides, oxides and soaps help to prevent such decomposition since these compounds act as heat-stabilizers.

³ "Geon" has been selected as the trade name for polyvinyl chloride resins produced by the B. F. Goodrich Co. The name "Koroseal" will be used by the Industrial Products Division of the Goodrich Co., while other fabricators of "Geon" will use other trade names.

If desired, the plasticized polyvinyl chloride may be dissolved in suitable solvents for solution application. Cyclohexanone and isophorone are the only solvents which can be used satisfactorily at room temperature, while dioxan, mesityl oxide, ethylene dichloride and chlorobenzene can be used at elevated temperatures.

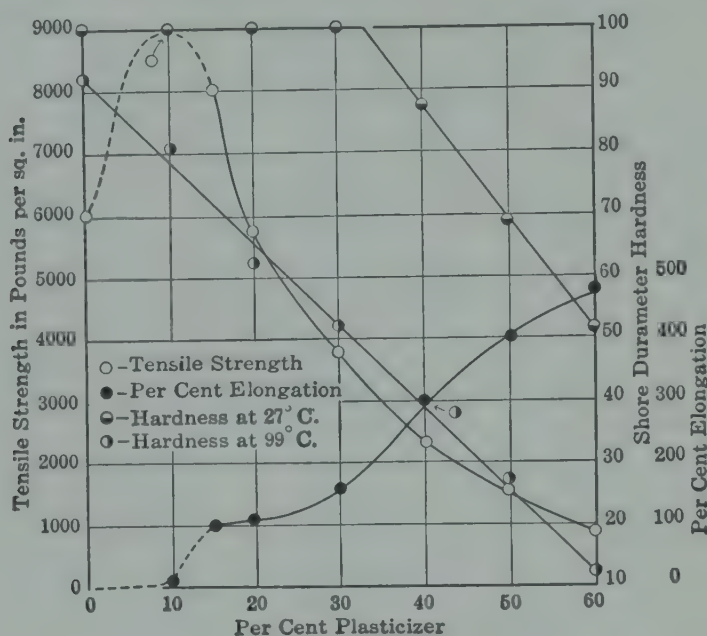


FIG. 15.1. Effect of varying amounts of plasticizer on tensile strength, elongation and hardness of Geon compounds. (Courtesy of Chemical Division, The B. F. Goodrich Co.)

Properties and Applications.—As a consequence of its poor solubility polyvinyl chloride is rarely used in solution form. The important applications of this plastic base depend upon the fabrication of extruded and molded goods. These products are characterized by extreme toughness, flexibility and resiliency. When properly plasticized (Geon type), the mechanical strength factors are favorable and, aside from the tear resistance, which is poor, an excellent rubber-like product may be obtained. These products also have excellent resistance to water and low flammability. In fact, polyvinyl chloride and polyvinylidene chloride are superior to all other vinyl polymers in these two respects. This is not surprising because other polychlorinated compounds such as carbon tetrachloride and chlorinated wax are not only insoluble in water but also are non-flammable. The chloride, in addition, is very resistant to swelling and disintegration by mineral and vegetable oils, also to aging and weathering. Tubing made from plasticized polyvinyl chloride is used for the

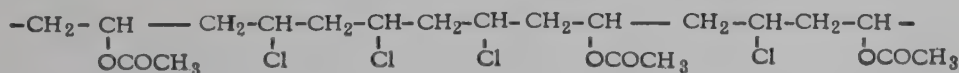
transfer of chlorine gas, ozone and sulfur monochloride, and is far superior to natural rubber for such purposes.

Cable coatings, gaskets, metal tank linings, packaging foil, chemically resistant finishes, toilet articles, shower curtains, raincoats, tableware, show parts and decorative novelties are additional uses which are typical of the expanding field of polyvinyl chloride plastic.

Polyvinyl chloride is available commercially as "Vinylite" polyvinyl chloride and as Geon.

POLYVINYL CHLORIDE-ACETATE COPOLYMER

Manufacture.—As has been stated above, polyvinyl chloride is hard, difficultly soluble and is used principally in molding and extrusion compositions, while polyvinyl acetate is relatively soft, readily soluble and is used chiefly in solutions or emulsions. Obviously, there are many possibilities in the plastics industry for materials having properties intermediate between those of polyvinyl chloride and polyvinyl acetate. Mixtures of the two polymers show poor compatibility and do not exhibit any worthwhile properties. In order to obtain the desired intermediate properties it is necessary to cause mixtures of vinyl chloride and vinyl acetate to copolymerize. It should be emphasized that the product is not a mixture of polyvinyl chloride and polyvinyl acetate. Each of the polymeric molecules contains vinyl chloride units and vinyl acetate units, e.g.,



The experimental conditions necessary to cause copolymerization are similar to those used for the polymerization of the pure monomers. Mass polymerization may be used, though solution and emulsion polymerization are more commonly employed. Benzoyl peroxide, acetyl benzoyl peroxide, tetraethyllead and ultra-violet light may be used as catalysts. The activity of peroxide catalysts can be enhanced by the addition of 0.25–2.0% of acetic anhydride or acetic acid.

Although less work has been done on the determination of the structure of these copolymers than in the case of polyvinyl chloride, the available data indicate that there is a chance arrangement of vinyl chloride and vinyl acetate units in the chain and that they have a "head-to-tail" (1,3) orientation. Marvel and co-workers found that the fraction of chlorine left in the polymer after treatment with zinc corresponds very closely with that calculated if a random introduction of vinyl chloride and vinyl acetate units into the growing

chain occurs and all have a 1,3-arrangement. This observation is correct in the case of copolymers having 60% or more of vinyl chloride in the molecule. When vinylite copolymers having 20–37% vinyl chloride are dehalogenated with zinc, the fraction of chlorine left is very much lower than the calculated fraction. One possible explanation is that vinyl chloride units enter the growing chain more rapidly than would be considered probable and consequently there are more chlorine atoms in 1,3-positions, not interspersed with acetate radicals, than would be expected.

Another very interesting observation made by Marvel and co-workers is that the first polymeric molecules formed contain a higher percentage of vinyl chloride units than the percentage of vinyl chloride in the mixture of monomers. These results were obtained by polymerizing different samples of the same mixture under the same conditions but for different periods of time before interrupting the polymerization. In one set of experiments, a monomeric mixture containing 12.48% of chlorine was 49% polymerized after 24 hours and the polymer contained 17.65% of chlorine. Since the chlorine content after complete polymerization is the same as that of the monomeric mixture, it follows that approximately half of the polymeric molecules formed must contain about 7% of chlorine. It is interesting to note, in this connection, that while vinyl chloride units are used up more rapidly than vinyl acetate units in copolymerization, pure vinyl acetate polymerizes more rapidly than pure vinyl chloride under the same experimental conditions.

Although the copolymer is a mixture of molecules which may have widely differing structures, it has been found possible to make a number of commercial polymers with different properties. For example, such properties as hardness, flammability, refractive index and resistance to moisture and chemicals vary with the percentages of monomers used. These copolymers are made from monomeric mixtures containing 80–95% of vinyl chloride.

The degree of polymerization may be altered by varying the experimental conditions such as temperature, solvent, dilution and catalyst. In this way, such properties as tensile strength, elongation, impact strength, and solubility may be widely varied. Thus, the factor of average molecular weight plays its role in determining the ultimate application of the plastic. Lacquer formulations require low molecular weight polymers; molding compounds are produced from high molecular weight products. Table IV-15 gives the trade symbol, percentage composition and approximate molecular weight of several commercial copolymers.

TABLE IV-15^a

Resin	Per Cent Vinyl Chloride	Ave. Mol. Wt.*
VYLF	85-88	6,000
VYHH	85-88	10,000
VYNS	88.5-90.5	16,000
VYNW	93-95	24,000


^a Vinylite Resins, Carbide and Carbon Chemicals Corp., New York, 1942.

* Approximate values, as determined by the Staudinger viscosity method.

Compounding and Fabrication.—The formulations used with this class of plastics depend upon the copolymer used and the application for which it is intended. In general, less plasticizer is required than is used with polyvinyl chloride, because of the internal plasticization afforded by the vinyl acetate units present in the chain. The amount of plasticizer may be varied, however, over a wide range and the stock produced may thus be fabricated into any form ranging from rigid rods and tubes to elastic film or flexible fiber. The class of plasticizers applied to polyvinyl acetate may also be used in conjunction with the copolymers. Dioctyl and dibutyl phthalates, di-butyl "Cellosolve" phthalate,⁴ "Cellosolve" ricinoleates, glycerol esters, tricresyl phosphate, camphor, and triacetin are typical examples of suitable plasticizing agents. A study of the effect of numerous plasticizers on the properties of the vinyl chloride-acetate copolymers has been made by Reed.⁵ The properties of the plasticized stock may then be changed by incorporation of a filler. These are used as required, and altered for specific properties, in order to extend the base resin, or stiffen the final material. Suitable pigments, dyes and mold lubricants can also be added.

In order to stabilize the copolymer so that it will not decompose when heated in a mold or baked in the form of a film on a metal surface, "heat stabilizers" are frequently incorporated into the resin. One of the best of these is the commercial preparation "Blue Lead," which consists of a mixture of basic lead sulfate, lead sulfite, lead sulfide, zinc oxide and a very small amount of carbon. Other heat stabilizers are such compounds as calcium carbonate, oxide or

⁴ "Cellosolve" is the trade name used for monoalkyl ethers of ethylene glycol.

The formula for di-butyl "Cellosolve" phthalate is  $\text{COOCH}_2\text{CH}_2\text{OC}_4\text{H}_9$
 $\text{COOCH}_2\text{CH}_2\text{OC}_4\text{H}_9$

⁵ Reed, *Ind. Eng. Chem.* **35**, 896 (1943).

hydroxide, calcium stearate and organic amines. The amount of heat stabilizer used is generally 1–2%.

The compounded resins are available commercially in the form of granules. These may be obtained by grinding the compounded resin. An interesting method of obtaining the powdered resin is by spraying fine droplets of a solution of the resin into another spray of a liquid which is not a solvent for the resin, but which is miscible with the active solvent. The resin is precipitated in a finely divided state. The compounded granules are used for molding or extrusion purposes. Fabrication of the unplasticized copolymer by compression molding requires temperatures of 120–145° C., and pressures of 1500–2000 lbs. per sq. in., followed by cooling in the mold to 32° C. For the compression molding of the plasticized copolymer, lower pressures of 500–1000 lbs. per sq. in. may be used. When the copolymers are used for injection molding, slightly higher temperatures and much higher pressures, 15,000–20,000 lbs. per sq. in., are employed. The best copolymers for use in injection molding are those having a molecular weight of 9,500–10,500 and containing 85–87% of vinyl chloride units.

The resin can be extruded in the form of rods, tubing, sheets and films. The sheets and films are available commercially in either plasticized or unplasticized form, colored or colorless, transparent, translucent or opaque. The copolymer sheets are obtained by mixing the "Vinylite" resin, pigment and opacifier in a heated mixer until the mass has a dough-like consistency. The mixture is milled on a two-roll mill until it is uniform, and then put in a calender mill, from which it emerges as a continuous sheet of any desired thickness. Rigid, unplasticized sheets are made from copolymers containing 88–90% of vinyl chloride and having a molecular weight of 15,000–16,000. These rigid sheets are manufactured in thicknesses of 0.010 to 0.250 inch. Flexible sheeting is made from copolymers containing 93–95% of vinyl chloride and which have a molecular weight of approximately 24,000. These flexible sheets are manufactured in thicknesses of 0.003–0.040 inch, while cast films made from the same copolymer are available in thicknesses of 0.001–0.005 inch. The finished article is made from these sheets and films by warming the resin until it can be shaped or cut readily and then allowing it to cool while held in the desired shape. Figures 15.2 and 15.3 illustrate two methods of shaping copolymer sheets.

Plasticization can also be achieved by dissolving the copolymer in a suitable solvent or mixture of solvents. The copolymers decrease in solubility as the vinyl chloride content or the molecular weight

increases. Although ketones, esters, ethers and chlorinated hydrocarbons may be used as solvents, those most frequently used are ketones such as 2-butanone, cyclohexanone, isophorone and mesityl oxide. Nitroparaffins are also satisfactory solvents. Aromatic hydrocarbons are commonly used as diluents or thinners for these solutions. The copolymers used for coatings applied in solution form have a molecular weight of 8500–9500 and contain 85–87% of vinyl

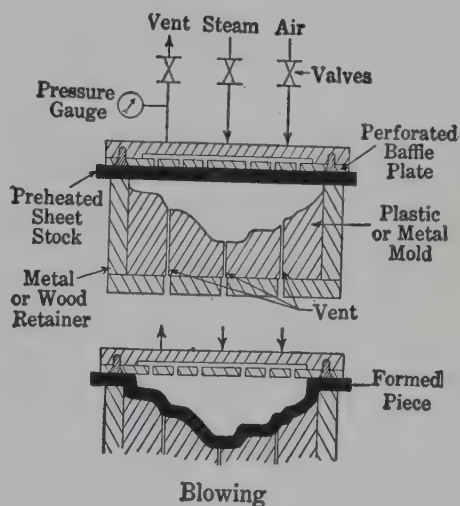
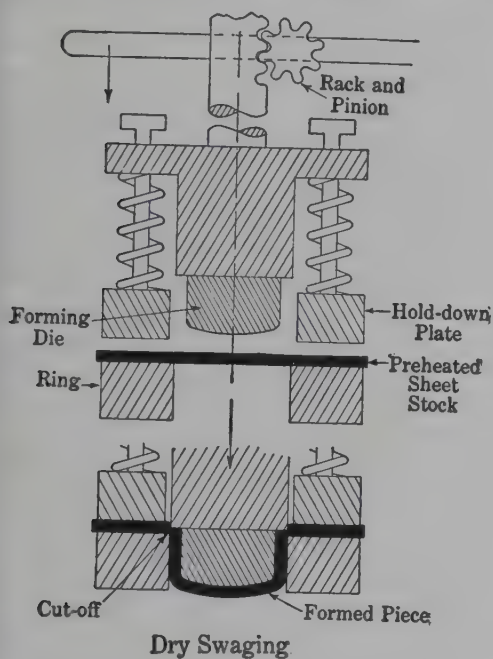


FIG. 15.2. Typical fabrication method used for the shaping of "Vinylite" sheet stock. (Courtesy of Carbide & Carbon Chemicals Corporation.)

FIG. 15.3. Typical fabrication method used for the shaping of "Vinylite" sheet stock. (Courtesy of Carbide & Carbon Chemicals Corporation.)

chloride units. In solubility applications, the copolymer plastics are notorious for their *thixotropy*. With each solvent blend, all types of copolymers reach a definite point at which gelling on standing undisturbed may occur. Higher concentrations in excess of this thixotropic range exhibit a permanently gelled condition. As a consequence, these materials are often spoken of as having "no high viscosity." By a variation of solvent blends—ketones and aromatic hydrocarbons, or ketones, esters and aromatic hydrocarbons—proper regulation of evaporation rates and suitable viscosities may be obtained. It is claimed that a solution of the copolymer in nitromethane, diluted with toluene, has less tendency to gel, and consequently flows more easily, than solutions in other solvents.

One of the most interesting fabrications of the "Vinylite" copolymer is the formation of a synthetic fiber known as "Vinyon." For this purpose, a copolymer having a molecular weight of approximately 20,000 and a vinyl chloride content of 88–90% is used. The resin is dissolved in dry acetone without the addition of any plasticizer, and the solution or "dope" thus formed is adjusted to a resin content of 25% or less.⁶ The resin is dispersed in a mixer or kneader at 50° C.; this operation may require as long as 12 hours. The resulting "dope" is a clear, viscous liquid which flows slowly at 50° C., but forms a gelatinous, non-flowing plastic mass at room temperature. This high viscosity appears to be a desirable feature so far as the ultimate properties of the fiber are concerned. The "dope" is filtered at 50° C., by means of a gear pump, using a pressure of 200–500 lbs. per sq. in. The filtered "dope" is de-aerated by standing for 24 hours at 50° C., usually with a partial vacuum above the solution. It is then spun in the same way that cellulose acetate filaments are spun, by forcing the solution through very small holes in a stainless steel die. The drying chamber for the removal of the solvent must be longer than that used with cellulose acetate because of the greater tendency of the "Vinyon" filament to retain the solvent. A stream of water heated to above 50° C., is played on the thread at the take-up bobbin. This serves the double purpose of removing the remaining acetone and also delustering the filaments. Before further processing, the filaments are allowed to age on the bobbins for 12 hours at room temperature or for 2–5 hours if immersed in water heated to 65° C. Water serves as a lubricant for the various operations involved in forming the finished yarn and prevents the development of a static electrical charge on the yarn. After twisting the individual filaments together to form the yarn, it is stretched 75–180%. The stretching is done by immersing the spool from which the yarn is to be stretched in an aqueous solution of a suitable wetting agent and winding the yarn onto a spool which is rotating faster than the unwinding spool. The desired stretch is usually obtained in two or more stages. The stretched yarn can be "set" by immersing it in water at a temperature of about 75° C. for 2–3 hours.

Properties and Applications.—The characteristics of the copolymer plastics are typical of what might be expected as a consequence of the fact that they are composed of vinyl chloride and vinyl acetate units. By the formation of a new compound containing both vinyl

⁶ Rugely, Feild and Coulon, U. S. Patent 2,161,766 (1939).

chloride and vinyl acetate units, the desirable features of high mechanical strength (characteristic of polyvinyl chloride) and good general solubility and compatibility (characteristic of polyvinyl acetate) are obtained.

The copolymers exhibit excellent resistance to water, salt solutions, acids, alkalies, alcohols, animal, vegetable and mineral oils. Poor resistance is encountered with ammonium hydroxide, ketones, esters, aldehydes, aromatic hydrocarbons and certain organic acids. The water absorption may be as low as 0.05% when immersed in

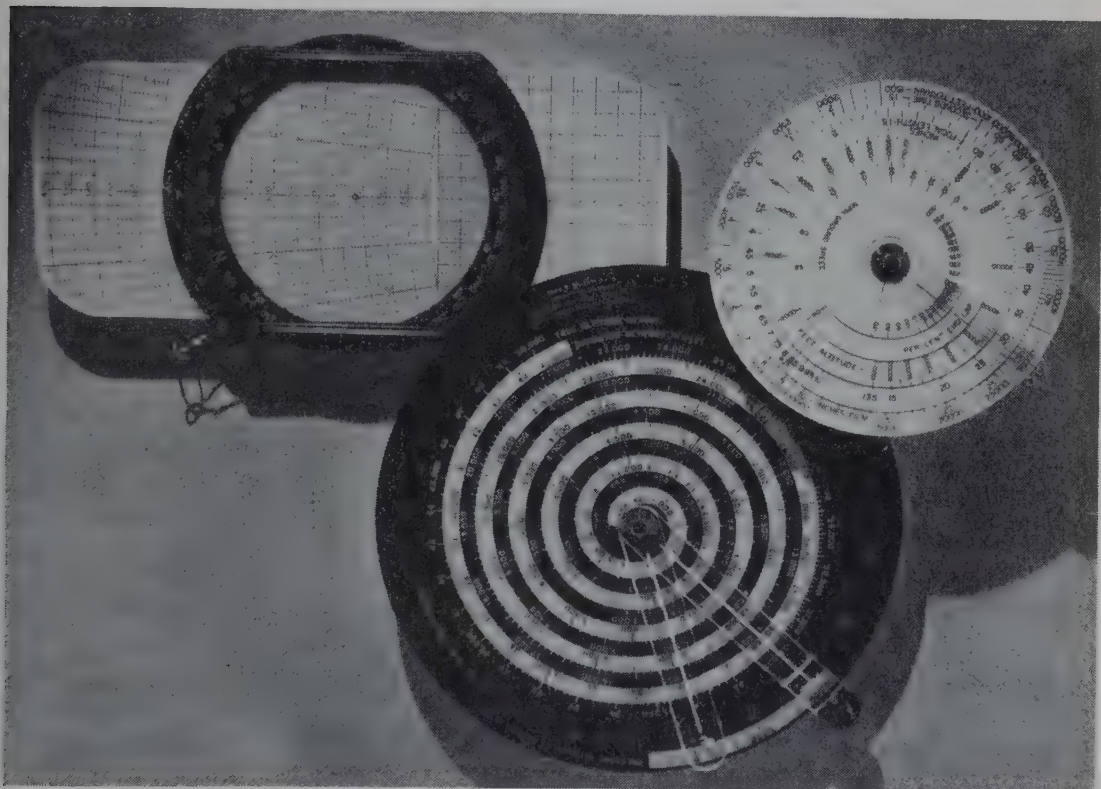


FIG. 15.4. Navigation instruments made from "Vinylite." (Courtesy of Plastics Division, Carbide & Carbon Chemicals Corp.)

water at 25° C. for 168 hours. As might be expected, the lowest water absorption values are obtained with copolymers containing a high percentage of vinyl chloride units. The low water absorption accounts for the excellent dimensional stability of the copolymer. This dimensional stability under all sorts of weather conditions is of great value in some of the applications of unplasticized "Vinylite" sheets, e.g., watch crystals, drawing instruments, calculating and navigating instruments (Figure 15.4), radio and refrigerator dials,

aircraft windows, phonograph records (Figure 15.5), bookbindings and various advertising novelties.

Sheets obtained from highly plasticized copolymer resins are characterized by their toughness, flexibility, elasticity and excellent resistance to tearing, scuffing and abrasion. They can be folded

repeatedly without cracking. Some sheets can be stretched up to 300% of their original length. This plasticized product is used for making articles of wearing apparel such as belts, suspenders and parts of shoes (Figure 15.6). A plasticized film is very satisfactory for use in making raincoats, sport jackets, umbrellas, shower curtains and similar water-resistant articles. Because of its excellent moisture resistance, the plasticized copolymer is used in making flexible bags to protect rifles, sub-machine guns and binoculars. It is also used as a replacement for rubber in the making of hospital sheeting and gloves. The "Vinylite" film is also of value in packaging food

and, because of its transparency, in the packaging of a great variety of articles.

The copolymer is used extensively in coating paper. This is done by calendering a 0.002 inch layer of plasticized "Vinylite" film onto a thin sheet (usually 0.003 in.) of paper. The resin is firmly bonded to the paper and the product is widely used as a liner for closures for all sorts of products, including foods. This is possible because of the fact that the copolymer is odorless, tasteless, non-toxic, and has excellent resistance to moisture. Cloth coated with a highly plasticized "Vinylite" copolymer is used in making shelter tents for aircraft and personnel in very cold climates. These tents consist of two layers of the coated cloth with three inches of glass wool between them. Even at -60°F. , the plastic-coated cloth remains flexible.

Molded "Vinylite" objects are strong, do not warp and have good dimensional stability. Combs, brush handles, dentures, floor tiles,



FIG. 15.5. Phonograph records made from "Vinylite." (Courtesy of The Soundsciber Corporation.)

shoe heels and shanks illustrate the types of materials that can be obtained by molding procedures.

In addition to the "Vinylite" sheets discussed above, tubing, window-sealing strips, and wire coatings can be obtained by extrusion of the properly compounded polymer. For the coating of wire,

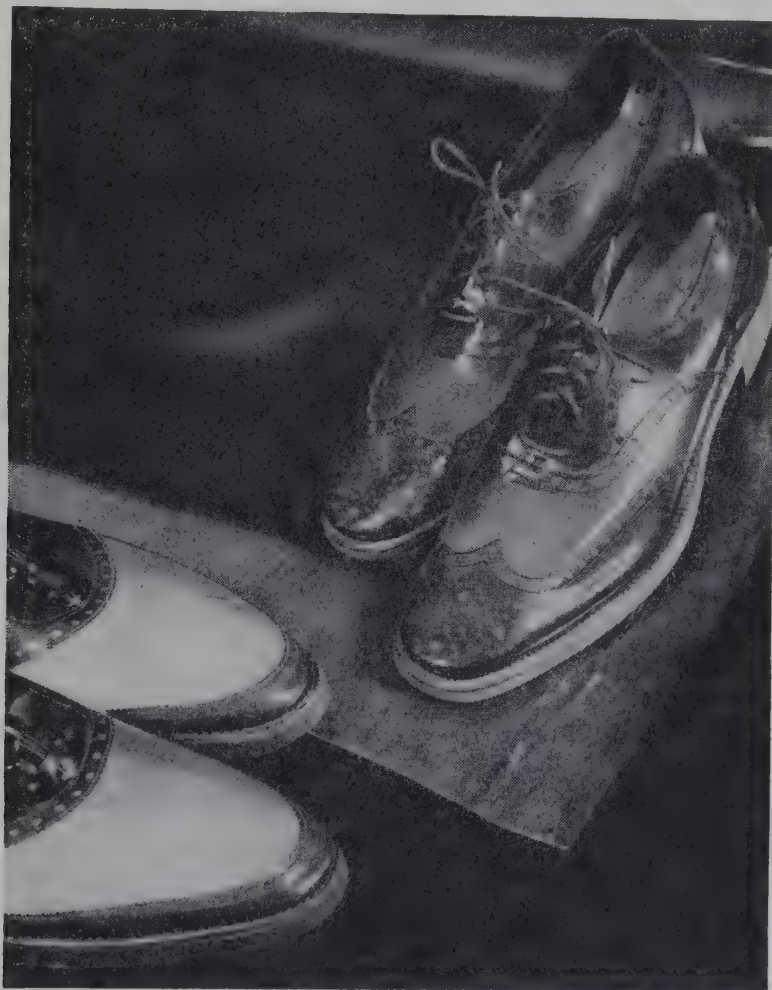


FIG. 15.6. Shoe uppers made from plasticized "Vinylite." (Courtesy of Plastics Division, Carbide & Carbon Chemicals Corp.)

polymers having molecular weights of 20,000–22,000 and containing 95% of vinyl chloride units are plasticized on a roll mill with various plasticizers to form a rubber-like mass. This plasticized resin is extruded as a continuous coating around the wire and may have any desired thickness. The coating has excellent electrical properties and is superior to rubber in resistance to moisture and chemicals. The non-flammability of "Vinylite" wire coating is also of great

practical importance. It can be obtained in any color, either opaque or transparent. By varying the concentration of plasticizer, different degrees of hardness may be obtained. Furthermore, by varying the nature of the plasticizer, it is possible to obtain a coating which is very resistant to oils or one which does not become brittle at low temperatures. A few satisfactory plasticizers for "Vinylite" copolymers at low temperatures are triethylene glycol dipelargonate, di-butyl "Cellosolve" sebacate, tri-butyl "Cellosolve" phosphate and tri-2-ethylhexyl phosphate.

Solutions of the copolymer are widely used to deposit surface coatings on metal, concrete, asbestos board, cardboard and paper. Most of the solvent is allowed to evaporate and then the material is baked in order to remove the remaining solvent and produce the maximum adhesion. It is desirable to bake the film on steel at temperatures of 175–205° C. These films on metal surfaces are widely used as linings for tanks and cans. Since the films are odorless, tasteless, non-toxic and impervious to the action of many chemicals, these objects can be used for the storage and transportation of foods and chemicals. An improved copolymer ⁷ for use in coatings which will dry simply on exposure to air at ordinary temperatures is obtained by using about 1% of maleic acid along with the vinyl chloride and vinyl acetate and copolymerizing the mixture. The presence of free carboxyl groups increases the adhesion of the film to the metal surface and yet there are not enough carboxyl groups to cause corrosion of the metal surface. Baking at a low temperature speeds the removal of the solvent and also improves the adhesion to the metal surface.

Paper, felt, or other fabric which has been impregnated with a solution of the copolymer may be shaped by heat and pressure. These shapes will be retained when the material cools. For example, felt can be stiffened with the copolymer resin to make box toes of shoes. Starchless collars are collars which have been impregnated with a copolymer resin. After laundering, ironing and cooling, they regain their original shape and stiffness, even though no starch is used.

Since "Vinyon" fiber is made from the copolymer without the use of any plasticizer, it is not surprising that it is impervious to the action, at room temperature, of such agents as mineral acids, alkalies, aqua regia, hydrogen fluoride, salt solutions, ammoniacal cuprous oxide, alcohols, and mineral oils. It is soluble in ketones and is either softened or dissolved by esters, halogenated hydrocarbons,

⁷ Doolittle and Powell, *Paint, Oil and Chemical Review*, 107 (7), 9 (1944).

aromatic hydrocarbons, ethers and certain amines. It is water-repellant, though the surface can be wetted by detergents. It is not attacked by bacteria, molds, fungi or mildew. It chars when placed in a flame, but it does not burn. The tensile strength of "Vinyon," 20,000–80,000 lbs. per sq. in., is directly proportional to the extent of stretching it has undergone. Since it is not affected by water the tensile strength in water is the same as when it is dry. The specific gravity of the yarn is 1.34–1.36. Without special treatment, the yarn has a bright luster, but this can be dulled, as in the case of nylon and cellulose acetate, by adding suitable finely divided white pigments to the spinning "dope." "Vinyon" can be dyed with water-insoluble acetate rayon dyestuffs by using "assistants" such as *o*-hydroxybiphenyl. The yarn is also an excellent electrical insulator.

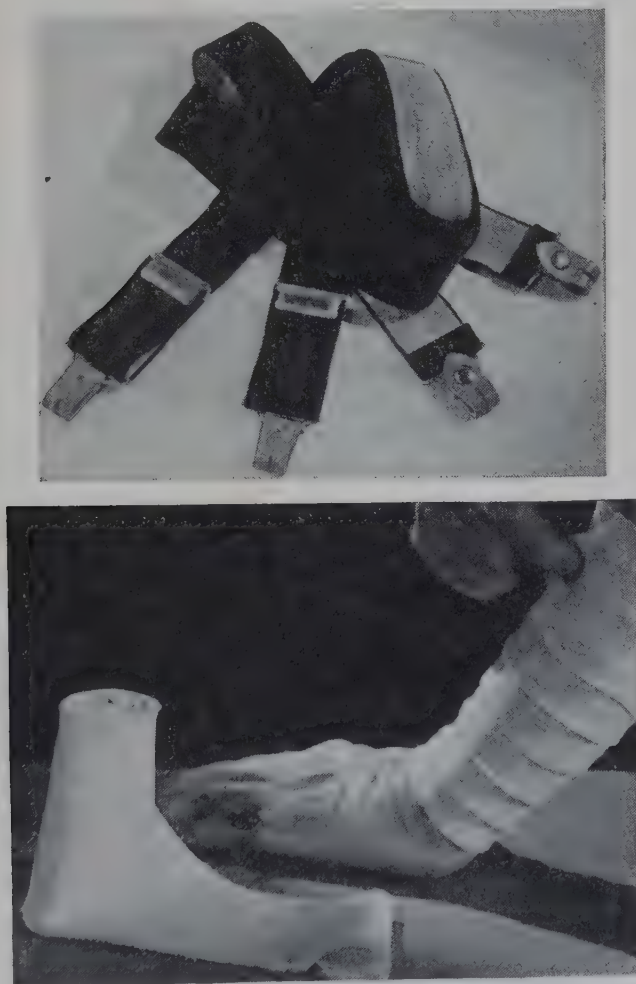
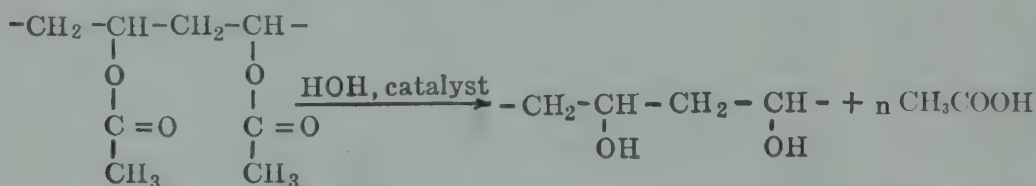


FIG. 15.7. Suspenders and bandage material made from "Vinyon." (Courtesy of Plastics Division, Carbide & Carbon Chemicals Corp.)

"Vinyon" is used in making cotton, wool and glass felts, in which the thermoplastic resin acts as a binder. Because of its imperviousness to so many substances, it has found extensive use as an industrial filter cloth. When woven into cotton, wool or rayon goods and heated properly, it provides crease permanency and crease resistance. It is also used in making fish nets, shower curtains, bathing suits, waterproof clothing, alkali- and acid-resistant clothing, sailcloth, umbrella fabrics, tent and tarpaulin materials, shoe linings, braids, hosiery, knit fabrics and fireproof awnings and curtains. Typical applications are shown in Figure 15.7. The greatest limiting factor in the use of "Vinyon" as a general textile fiber is that it becomes soft at such low temperatures. At 75° C., it undergoes about a 12% shrinkage; at 80° C., there is a noticeable tendency of the filaments to adhere to one another; at 135–140° C., definite tackiness develops. However, it has already found an extensive list of uses, and other uses will be found as the quality of the product is improved.

POLYVINYL ALCOHOL

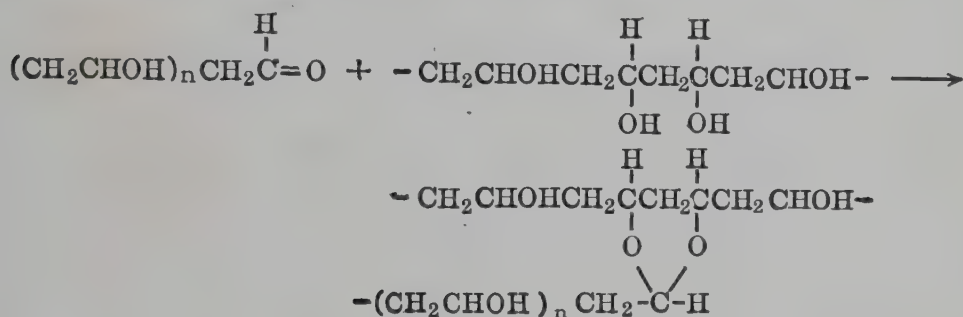
Manufacture.—Since vinyl alcohol does not exist,⁸ polyvinyl alcohol must be made by an indirect method. Either polyvinyl acetate or polyvinyl chloride can be hydrolyzed to form polyvinyl alcohol. The acetate is generally used because it is more soluble and hence easier to manipulate than the chloride. Hydrolysis may be carried out in an organic solvent under the influence of either an acidic or basic catalyst. The reaction mixture is usually refluxed for a definite period of time, depending on the extent of hydrolysis desired. As the reaction proceeds, however, the replacement of acetate groups by hydroxyl groups is accompanied by the gradual development of an insoluble slurry as polyvinyl alcohol separates from the solvent used. The precipitated plastic may be filtered, washed, and dried. The reaction is represented as follows:



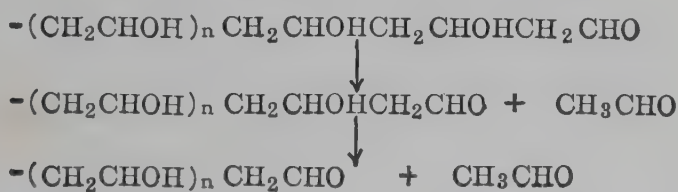
Since several different forms of polyvinyl acetate are available, having different molecular weights, the molecular weight, and conse-

⁸ The formula for vinyl alcohol, $\text{CH}_2=\text{CHOH}$, represents it as a tautomeric form of acetaldehyde, CH_3CHO . All attempts to make vinyl alcohol have resulted in the formation of acetaldehyde.

quently the properties of the polyvinyl alcohol obtained will depend upon the particular polyvinyl acetate hydrolyzed. From the equation given above, it would be assumed that the degree of polymerization of the polyvinyl alcohol would be the same as that of the polyvinyl acetate used. However, Marvel and Inskeep⁹ found that the degree of polymerization of the polyvinyl alcohol produced might be larger or smaller than that of the polyvinyl acetate used. An explanation⁹ of these unexpected and irregular results is possible if the polyvinyl alcohol molecules have a terminal aldehyde group. The aldehyde group should be capable of forming an acetal with the hydroxyl groups of another molecule of polyvinyl alcohol.



This would account for the formation of polyvinyl alcohol molecules having a higher degree of polymerization than that of the polyvinyl acetate used. Products with a lower degree of polymerization may be formed by a reverse aldol condensation causing the successive removal of acetaldehyde molecules from the chain.



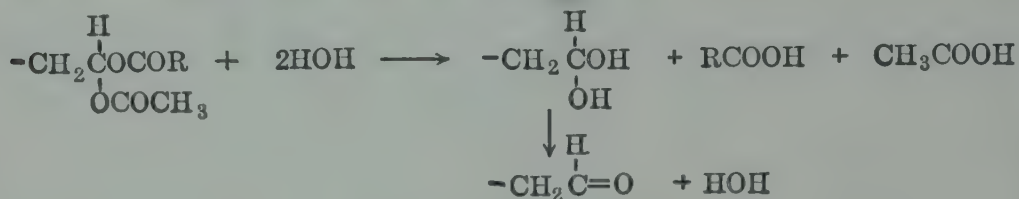
Evidence for the existence of an aldehyde group was found when a sample of polyvinyl alcohol yielded a 2,4-dinitrophenylhydrazone when treated with 2,4-dinitrophenylhydrazine. If the terminal groups of the polymer chain are fragments of the catalyst,¹⁰ it is entirely possible, when a peroxide is used as a catalyst, that the terminal grouping in a polyvinyl acetate molecule may be



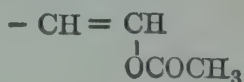
⁹ Marvel and Inskeep, *J. Am. Chem. Soc.* **65**, 1710 (1943).

¹⁰ Price, Kell and Krebs, *J. Am. Chem. Soc.* **64**, 1103 (1942).

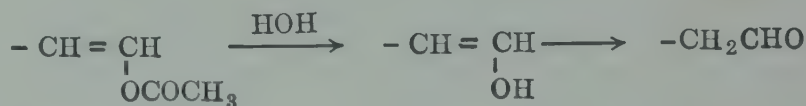
depending upon whether an OH group or an OCOR group is obtained from the catalyst. The terminal grouping in formula (1) might split off a molecule of acetic acid, so that an aldehyde group may actually be present in the polyvinyl acetate molecule. If that configuration is stable in the acetate polymer, hydrolysis would certainly yield an aldehyde group. Hydrolysis of the terminal grouping represented in formula (2) would also yield an aldehyde group.



However, it should be pointed out that when *p*-bromobenzoyl peroxide was used as the catalyst in the polymerization of styrene, Price, Kell and Krebs did not succeed in obtaining any *p*-bromobenzoic acid when the polymer was subjected to hydrolysis. Consequently they assumed that the *p*-bromophenyl radical was the terminal group of the polymer chain rather than the *p*-bromobenzoate radical. Still another possible explanation, also proposed by Marvel and Inskeep, is to assume that a disproportionation of the terminal group occurs when chain growth ceases, forming an enol acetate,



Hydrolysis of such a terminal group would produce a vinyl alcohol structure which would rearrange immediately to form an aldehyde group.



Another factor of importance in determining the properties of the polyvinyl alcohol produced is the degree of hydrolysis. The so-called "completely hydrolyzed" product contains approximately 5% of residual acetate groups. The percentage of acetate left in the macromolecule may range upward from this minimum. When dealing with polymers of comparable molecular weights, the lower the percentage of acetate left in the polymer, the greater the solubility in water, the greater the resistance to oils and the higher the softening point.

Compounding and Fabrication.—Polyvinyl alcohol, particularly the “completely hydrolyzed” type may be applied in the form of solutions, molding compounds and plastic sheets or tubes in pre-fabricated shapes. Since the “completely hydrolyzed” polyvinyl alcohol is soluble in water, aqueous solutions may be used. When making an aqueous solution, the powder is stirred into cold water until the mixture is smooth and homogeneous. The mixture is then heated, with stirring, to a temperature of 50–85° C., depending upon the polymer used, until the solution is clear. The polymer may also be compounded with suitable plasticizers (usually high molecular weight polyhydroxy alcohols, esters and amides) and the mixture used in solution. Polyvinyl alcohol solutions can be mixed with solutions or suspensions of rubber latex, casein, soy-bean protein, starch and dextrin.

When making a molding compound, fillers, plasticizers, pigments and other modifying agents may be added. By varying the nature and amounts of these added materials and by varying the processing technique, it is possible to obtain different values for such properties as hardness, abrasion resistance, resiliency, translucency and tensile strength. Molding is usually carried out at temperatures of 120–145° C., and pressures of 250–1000 lbs. per sq. in. The compounded material is heated for about ten minutes and is then cooled to 100° C., before releasing the pressure and ejecting the object from the mold. Rubber-like gaskets, washers and diaphragms are made by the usual molding process. One of the most practical formulations of polyvinyl alcohol is known as “Resistoflex.” This rubber-like product, which is a solid colloidal solution, consists essentially of plasticized polyvinyl alcohol. The plasticizers used are polyhydroxy alcohols, acid amides and aminohydroxy compounds. The incorporation of dibasic acids, chromium compounds, zinc-ammonia compounds or copper-ammonia compounds into the molding compound improve the water resistance of the resulting product. These plasticized compositions are extruded as tubes, rods, sheets and threads.

Properties and Applications.—Polyvinyl alcohol is a white, tasteless, odorless powder, and the films obtained from aqueous solutions or suspensions are colorless and transparent. These films are exceptionally tough and exhibit excellent resistance to mineral and vegetable oils, simple alcohols, esters, ethers and many other organic liquids. The films are, however, dissolved or softened by water, polyhydroxy alcohols and aminoalcohols. When the insolubilizing agents, dibasic acids, etc., listed above, are incorporated into these films, they are much more resistant to the solvent action of water.

Consequently, films of polyvinyl alcohol can be obtained in forms that are soluble in water at room temperature and also in forms that are insoluble in boiling water. Films of polyvinyl alcohol are used as tough, protective coatings for highly polished metal surfaces during fabrication, or shipment, providing excellent protection from scratches. The film can be removed simply by soaking the object in water for a few minutes.

Another interesting use of these films is as a protection for textile yarns. The film is put on for the weaving operations and is later removed by immersing the yarn in water heated to 65–70° C. The film dissolves and stays in solution even when the water is cooled. The film can also be removed safely during the dyeing process. A thin film of polyvinyl alcohol applied to glass prevents fogging when one side of the glass is exposed to high humidity on one side and low temperature on the other. This application is of value on automobile windshields and the windows of gas masks. Thin, transparent, flexible gloves can be made from polyvinyl alcohol.

Films of polyvinyl alcohol can be made sensitive to light by the incorporation of potassium or ammonium dichromate in the film. Such films are of value in photo-lithographic printing, because those portions of the film (usually deposited on a zinc plate) which are exposed to light are rendered water-insoluble, while the unexposed portion is soluble. The insoluble portions remain to form the printing surface of the plate. In this connection, it is interesting to note that the properties of polyvinyl alcohol and its derivatives are claimed to be vastly improved by steeping them in solutions of compounds of metals of the sixth and eighth groups of the periodic table, either at room or elevated temperatures, with simultaneous exposure to light.

When paper is impregnated or coated with polyvinyl alcohol, it shows a marked increase in wet strength, with no appreciable decrease in the rate of absorption of water. This increased wet strength lasts for about forty seconds, which is sufficient for most purposes for which paper towels are used. Polyvinyl alcohol is also used in the making of glassine paper. It serves to make the paper transparent and also acts as a softening agent. Because of its excellent resistance to mineral, vegetable and animal oils, it is used for making paper and paper containers grease-proof.

Polyvinyl alcohol is an excellent adhesive and can be used alone or mixed with other adhesives such as starch, dextrin, casein, or rubber latex. It is especially valuable as an adhesive for the application of pigmented coatings to paper, cloth and leather. Increased

water resistance can be imparted by using the insolubilizers mentioned above. It is also used in making white shoe dressings. Because of its excellent film-forming ability, it prevents chalking of the white pigment.

Polyvinyl alcohol is useful as an emulsifying agent and possesses the added advantage of functioning in a neutral or slightly acidic medium. One practical use of this fact has already been mentioned in connection with the emulsion polymerization of vinyl acetate (see p. 274). It serves as an emulsifying and thickening agent in the manufacture of brushless shaving creams and various cosmetic creams.

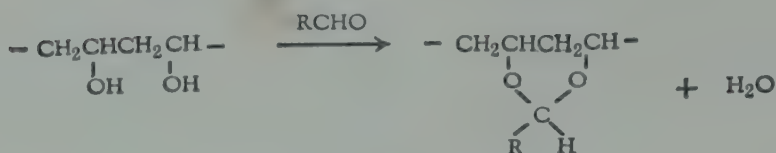
The Resistoflex forms are noted for their high tensile strengths, tear resistance, abrasion resistance, aging characteristics, excellent flex resistance and low gas permeabilities. Resistoflex is so flexible that it can be tied into knots. It is used as piping in fuel, brake and lubrication systems of automobiles, airplanes and Diesel engines, also for conveying solvents, mineral and vegetable oils. Since Resistoflex compositions are moderately resistant to heat, they can be used as tubing for the spraying of hot lacquers. When sound waves are transmitted through Resistoflex tubing, there is a minimum of distortion and very little absorption by the tubing. Consequently, this material finds a use wherever it is desirable to send sound through a flexible conduit.

Rubber-like products can also be obtained by heating polyvinyl alcohol with sulfur. The polyvinyl alcohol appears to be vulcanized and either soft or hard vulcanizates are obtained, depending upon the amount of sulfur used.

Threads of polyvinyl alcohol have been obtained not only by extrusion of a molding composition, but also by the extrusion or spinning of an aqueous solution into an organic solvent which is miscible with water. Acetone, cellosolve and ethyl lactate have been found to be satisfactory for this purpose. The threads are then treated with an acid chloride, such as thionyl chloride or phosphorus trichloride, in order to increase their resistance to solvents and the action of moisture.

POLYVINYL ACETALS

Manufacture.—Polyvinyl acetals are made by the interaction of polyvinyl alcohol with various aldehydes. The reaction is the same as the usual reaction between an aldehyde and an alcohol and may be represented as follows:



The low molecular weight aliphatic aldehydes are the only aldehydes that have been used to make commercial products, and of these, butyraldehyde, acetaldehyde and formaldehyde are the most valuable. In the manufacture of polyvinyl acetals, polyvinyl alcohol is not isolated. The formation of the acetal is carried out in the same solution in which the polyvinyl acetate is hydrolyzed. Methanol or acetic acid, containing small amounts of sulfuric acid, can be used as the solvent. The aldehyde is added at the beginning of the reaction, as soon as the polyvinyl acetate has dissolved. The course of the reaction can be followed by analyzing samples of the reaction mixture for aldehyde content.

The number of variations in the structure of the final polymeric acetal, and consequently the variations in properties, are very large, as will be evident from the following discussion. The first variable is the structure of the polyvinyl acetate used. It may consist chiefly of long chains, short chains or intermediate chains. In the second place, the extent of hydrolysis of the polyvinyl acetate to polyvinyl alcohol will play an important part in the final properties obtained in the acetal. It should be recalled that the possibility of the chain length increasing or decreasing during this hydrolysis introduces still another variation. The fourth variable refers to the extent of acetal formation. By varying the amounts of polyvinyl alcohol and aldehyde, it is possible to get a large or small proportion of acetal groups in the final molecule. The final plastic, therefore, may contain varying proportions of hydroxyl, acetate and acetal groupings. By altering these proportions, it is possible to vary such properties as softening point, viscosity, resistance to chemicals and mechanical strength.

Compounding and Fabrication.—The polyvinyl acetals are obtained as white powders which are mixed with plasticizers and frequently with other resins. Numerous high boiling esters such as the dialkyl phthalates, succinates and maleates have been used as plasticizers. In general, about forty parts of plasticizer are mixed with sixty parts of polyvinyl acetal to make an extremely tough, elastic product. These plasticized resins can be dissolved in suitable solvents or they can be emulsified in aqueous solution. It is interesting to note that polyvinyl formals dissolve in water. Polyvinyl acetal and

polyvinyl butyral are insoluble in water, but dissolve in methyl, ethyl, isopropyl and butyl alcohols, alcohol-ethers and dioxan.

For the preparation of molding compounds suitable for use in compression, injection or extrusion equipment, the polyvinyl acetal is compounded with plasticizers, fillers and other resins. By varying the nature and the amount of the modifying agents, products having different properties can be obtained. In order to improve the heat stability of these resins, small amounts of phenol, naphthol, quinol, hydroxylamine, amines, sodium thiosulfate and other compounds are added. The compounded, dough-like mass is then filtered through fine screens to remove any lumps and then forced into a mold or extruded in the form of a continuous sheet.

One of the latest compounding variations of the polyvinyl acetals is the introduction of thermosetting characteristics into the plastic by incorporation of a phenol-formaldehyde or urea-formaldehyde resin with the base plastic by milling. When cured by proper heating, the component parts interact to eliminate all thermoplastic tendencies. By this method, unusual characteristics of toughness, resiliency, and abrasion resistance have been produced. The resultant product is finding widespread use as a rubber replacement material which is of particular value in fabric coatings and molded goods.

Properties and Applications.—The resistance of polyvinyl acetals to organic solvents and to moisture is not as good as that of the "Vynlite" copolymers. It is extremely resistant to sunlight and does not discolor even when exposed for long periods of time to ultra-violet radiations. It is also very stable to heat up to about 100° C. Sheets of polyvinyl acetals are transparent and hence are used as packaging material.

The most widely used acetal is polyvinyl butyral. This substance, when properly plasticized, is probably the best material yet found for the interlayer in laminated safety glass. The tough, rubbery plastic sheet is placed between two sheets of glass and the "sandwich" is then subjected to high pressure. The plastic adheres so firmly to the glass surfaces that no other adhesive is required. Furthermore, it is so impervious to moisture that edge-sealing (necessary when certain other interlayers are used, in order to prevent moisture from weakening the adhesion to the glass) is unnecessary. Light transmission of this type of safety glass is thoroughly satisfactory, even though not as high as when polymethyl methacrylate is used. This plastic is very tough and that is the chief reason why it has proved so satisfactory in safety glass. Figure 15.8 demonstrates

what happens when a 16-pound bowling ball is dropped from a height of about four feet onto this type of laminated safety glass. The plastic yields but does not break. Furthermore, the plastic holds the shattered glass in place. Bullet-proof safety glass for use as the windshields of bombers and fighters is composed of six sheets of polyvinyl butyral laminated between sheets of glass. These windshields are 1.5 inches thick and will withstand a direct shot from a 50-caliber machine gun. An important advantage is that the toughness and flexibility of the plastic are retained even at the low temperature of -40°C . It also has excellent dimensional stability. Another interesting application is the production of waterproof clothing by inserting a sheet of polyvinyl butyral between two sheets of cloth.



FIG. 15.8. Sixteen pound bowling ball dropped onto laminated safety glass. (Courtesy of Libbey-Owens-Ford Glass Company.)

The excellent adhesive characteristics of polyvinyl butyral are utilized in the making of coatings and impregnants as well as adhesives. Coatings and impregnations may be applied either in the form of solutions, emulsions, or hot melts. The relatively high softening point, $120\text{--}200^{\circ}\text{C}$., and the tendency of the butyral to discolor above the softening temperature limit the number of hot-melt applications. As a thermoplastic adhesive, it is used with leather, rubber, paper, wood, glass and plastics.

Polyvinyl formals¹¹ can also be made from polyvinyl acetate and formaldehyde under conditions suitable for hydrolysis and acetal formation. In the only formals which have yet been marketed industrially, hydrolysis of the acetate is about 95% complete and most of the alcohol groups have reacted with formaldehyde. These resins can be plasticized effectively with dialkyl phthalates and mixtures of dialkyl phthalates and sebacates. They are soluble in a variety of solvents, e.g., chlorinated hydrocarbons, dioxan, organic acids and mixtures of polar and non-polar solvents. Polyvinyl formals are used in making lacquers, wire enamel, coatings, impregnations, plastic sheets, molded articles and as the interlayer in safety glass. The chief disadvantage of polyvinyl formals is that they are not very resistant to water.

Polyvinyl acetals made from acetaldehyde are similar to cellulose acetate with respect to solubilities, effective plasticizing agents and compatibility with other resins. They are used in making lacquers, adhesives, coatings, impregnations and molded articles, e.g., phonograph records.

The trade names for the polyvinyl acetals are: "Vinylite" Polyvinyl Butyral, Butacite, Butvar and Saflex for the butyraldehyde derivative, Formvar for the formaldehyde derivative and Alvar for the acetaldehyde derivative.

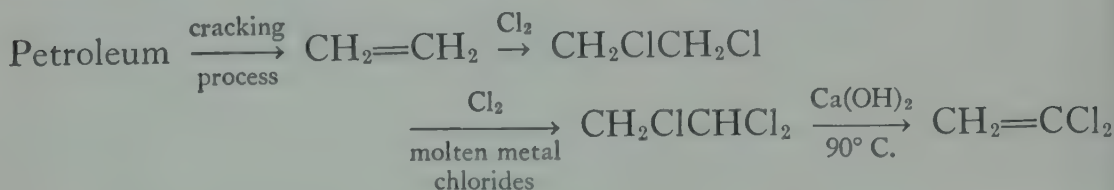
POLYVINYLIDENE CHLORIDE

This plastic, known commercially as either Saran or Vec, is rapidly becoming one of the most important thermoplastic polymers. The wide variations of properties obtainable with this polymer and its copolymers together with their ease of fabrication have contributed to their rapid rise in popularity.

Manufacture.—Polyvinylidene chloride is obtained by the polymerization of unsymmetrical dichloroethylene, also called vinylidene dichloride. This monomer can be obtained from ethylene dichloride by first chlorinating ethylene dichloride to form 1,1,2-trichloroethane. The chlorination process is carried out by forcing a mixture of 55–75 parts of chlorine and 100 parts of ethylene dichloride into the bottom of a molten bath of metal chlorides kept at a temperature of 300–425° C. Liquid mixtures of metal chlorides within this temperature range are selected from the following salts: aluminum chloride, ferric chloride, bismuth chloride, zinc chloride, potassium chloride and sodium chloride. Trichloroethane is then treated with lime in order

¹¹ Morrison, *Chem. and Ind.*, 1941, p. 392.

to remove one equivalent of hydrogen chloride, thereby forming vinylidene chloride. The formation of vinylidene chloride from petroleum may be represented by the following scheme:



Vinylidene chloride is a liquid having a boiling point of 31.7° C . The liquid has a tendency to polymerize on standing, and this tendency is greater with impure samples than with pure samples. In order to store the monomer for future use, stabilizers are added to prevent polymerization and oxidation. Numerous organic compounds have proved satisfactory for this purpose, including diarylamines (e.g., phenyl naphthylamines), diaryl alkylene diamines (e.g., diphenylethylenediamine), aromatic compounds having at least one phenolic hydroxyl group linked to the aromatic nucleus, thioethers, thioalcohols, thiophenols and other organic sulfur compounds. These stabilizers can be removed just before use by distilling the monomer. As will be pointed out later, some catalysts have been developed which are so effective that it is not necessary to remove the stabilizer before polymerizing. A totally different group of stabilizers consists of such inorganic compounds as concentrated sulfuric and nitric acids, iodine, sulfur monochloride and antimony chloride. These stabilizers are removed by shaking the monomer with aqueous alkali.

Vinylidene chloride can be polymerized by any of the methods used for the polymerization of vinyl compounds. Peroxides, principally benzoyl peroxide, metal alkyls and metal carbonyls, as well as mixtures of these compounds have been used successfully as catalysts. Chloroacetyl chloride and metallic copper appear to be effective aids to the principal catalyst. A superior catalyst mixture has been described as consisting of tetraethyllead, chloroacetyl chloride and spongy copper. This catalyst is so effective that it is not necessary to remove the stabilizer before polymerization. Another excellent catalyst is obtained by adding an alcoholic solution of uranium nitrate or uranium acetate to the monomer and exposing the solution to sunlight or light from a tungsten lamp. Exposure to light is necessary in this case in order to cause polymerization.

The monomer may be polymerized either with or without a non-polymerizable solvent such as *o*-dichlorobenzene, trichlorobenzene or ethylene dichloride. When a solvent is used, it is desirable to prevent

contact of the reaction mixture with air by covering the solution with a layer of water. This process yields an amorphous powder which can be molded easily. Furthermore, the product is more stable toward heat because of the absence of hydrogen chloride and phosgene, compounds which are often found in the polymer when no special precautions are taken to exclude contact with air. The properties of the polymer vary according to the degree of polymerization achieved. As in the case of other vinyl compounds, a low temperature of polymerization favors the formation of a high molecular weight product and a high temperature causes the formation of lower molecular weight polymers. The temperature used for polymerization of vinylidene chloride varies from room temperature to about 90° C. Products having substantially different properties can also be obtained by copolymerizing vinylidene chloride with other unsaturated compounds such as vinyl chloride, styrene, butadiene and acrylates. For example, a copolymer obtained from vinylidene chloride and vinyl chloride was found to be a white powder when polymerization was 20% complete. When polymerization was 40–50% complete, the product was a porous mass and when practically complete polymerization occurred, the product was a hard bone-like mass, which could, of course, be ground to form a molding powder. By varying the composition of the monomeric mixture from 5 to 30% of vinyl chloride, by varying the temperature of the polymerization from 25–40° C., and by varying the length of time permitted for polymerization, it was possible to obtain products having softening temperatures from 80–170° C. The more common commercial grades of polyvinylidene chloride and copolymers have softening temperatures of 120–140° C., and molecular weights of about 20,000.

In order to improve the heat stability of vinylidene chloride polymers and prevent discoloration and decomposition with the liberation of hydrogen chloride when heated, it is desirable to remove any catalyst residues, such as peroxides or peruranates. This can be done by washing the finely powdered polymer with an aqueous methanol solution of sodium bisulfite in a ball mill. This washing reduces the peroxides and peruranates so that the polymer does not show any test for peroxide.

Structure.—Because of the high proportion of polar constituents, the polymeric vinylidene chloride is easily oriented to the crystalline form. X-ray analysis has proved that the positions of polymeric molecules in this material may be changed relative to one another so that it can exist either in a crystalline form or an amorphous form.

In fact, commercial polyvinylidene chloride (Saran) may exist not only in the crystalline and amorphous states, but also in an oriented crystalline form. The x-ray diffraction patterns of these three forms are shown in Figure 15.9. The unusual feature of this plastic is the fact that the crystalline arrangement is the normal state. The possible existence of three states, however, has its resultant effect upon the variation of properties. The factor of mechanical strength is particularly dependent upon the physical condition of the plastic. The tensile strength, for example, may be increased from a representative value of 10,000 lbs. per sq. in. to 50,000 lbs. per sq. in., when crystallization occurs. Other mechanical properties such as impact strength and flex fatigue life increase proportionately.

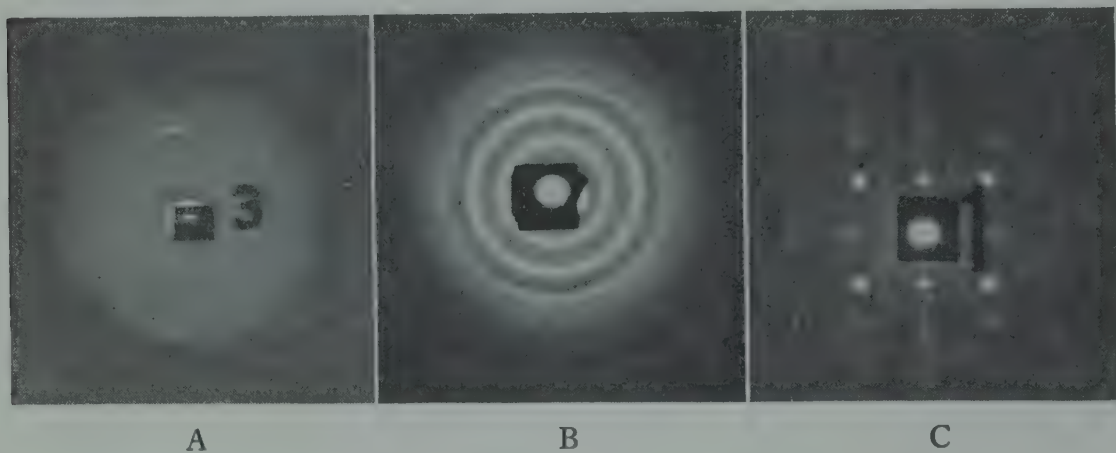


FIG. 15.9. X-Ray diffraction patterns of amorphous (A), crystalline (B), and oriented crystalline (C) forms of saran. (Goggin and Lowry, *Ind. Eng. Chem.* **34**, 328, 1942.) (Courtesy of The Dow Chemical Company.)

Compounding and Fabrication.—The compounding of polyvinylidene chloride and its copolymers for application in injection molding or extrusion processes is comparable to that used in the case of other vinyl polymers. The base resin may be mixed with plasticizers and fillers or it may be dissolved in a suitable solvent. Proper plasticization of these polymers has an important effect on the final properties. For example, a non-plasticized bar of polyvinylidene chloride showed a tensile strength of about 3500 lbs. per sq. in. Other bars, plasticized with polychloro derivatives of aromatic hydrocarbons and ethers, e.g., polychlorobiphenyl, polychlorobenzene, polychlorodiphenyl oxide, showed tensile strengths of 4700–5600 lbs. per sq. in. Plasticizers such as dibenzyl ether and other aralkyl ethers gave products with substantially higher impact values when compared with either the unplasticized polymer or a polymer plasticized with tricresyl phos-

phate. Other plasticizers which have been used successfully with these polymers include phenoxy- and butoxy-propylene oxides, styrene oxide, hexachloroethane and related compounds. The amount of plasticizer used is generally from 5–40%.

Suitable molding compositions can be obtained by incorporating with the base resin such fillers as wood flour, asbestos fibers, cellulose fibers and other finely divided inert materials. The compounding of these ingredients may be done (a) by mixing them together in the mold die, (b) by the use of masticating rolls, or (c) by adding the filler to the monomer mixture before polymerization.

The molding composition, made by mixing the polymeric resin and plasticizer with or without an inert filler, is usually fabricated either by extrusion or injection molding. Extrusion does not present any particular problem, although iron, steel and copper cannot be used for the hot zones of either extrusion or injection equipment. At temperatures above 130° C., these metals catalyze the decomposition of polyvinylidene chloride. Metals which can be used are magnesium alloys, nickel, Stellite 10 and Hastelloy B. Polyvinylidene chloride has a narrow softening range as shown in Figure 15.10. The crystalline nature of the plastic is the cause of the absence of a broad softening range characteristic of amorphous thermoplastic materials. However, it can be extruded very easily when it has been heated above this temperature. The plastic, when first extruded and cooled, is soft, weak and pliable, due to the amorphous condition produced when the molecules are "frozen" in an unoriented form. It gradually hardens on standing, as a result of crystallization of the polymer. By gently heating the extruded product, crystallization, and consequently hardening, may be achieved in a short time. See Figure 15.11. The plastic may be extruded in the form of rods, flexible tubing and pipe, tape and various items of wearing apparel such as suspenders and belts. The solid polymer may be further processed by such machining operations as sawing, drilling, punching and polishing.

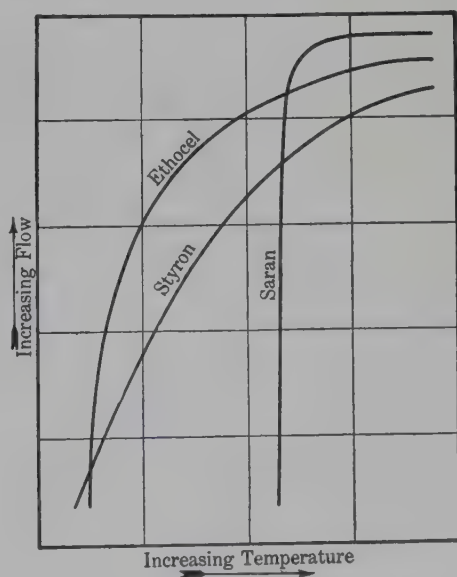


FIG. 15.10. Plastic flow vs. temperature of several thermoplastics. (Goggin and Lowry, *Ind. Eng. Chem.* **34**, 329, 1942.)

When Saran is used in injection molding machines, it is desirable for the molded object to be kept in a hot die (80–100° C.) for a short time (see Figure 15.11) in order to hasten crystallization and consequent hardening. The object can then be ejected from the hot die sooner and in a harder state than would be possible if the injection mold were kept at room temperature. Unlike most other thermoplastic materials, therefore, the use of a hot die shortens the length of time required for a complete cycle of operation and hence speeds up the manufacturing process.

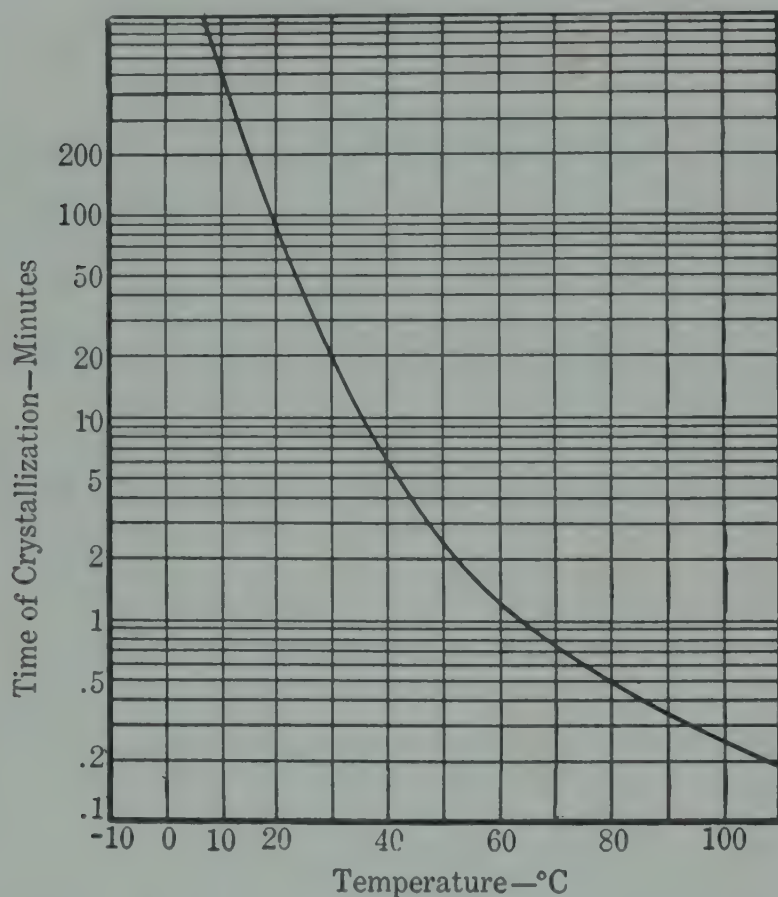


FIG. 15.11. Effect of temperature upon crystallization of Saran. (Goggin and Lowry, *Ind. Eng. Chem.* **34**, 330, 1942.)

A third method of fabrication involves the mechanical processing of the plastic in a super-cooled amorphous state. The polymer is extruded in the form of a filament or tape and cooled very rapidly (2–60 seconds) to room temperature. In this supercooled state the polymer retains an excellent degree of plasticity for a period of about two minutes and then gradually becomes (in about 60 minutes)

relatively non-plastic. In the supercooled condition, a pressure of 1000 lbs. per sq. in. is required for plastic deformation, whereas a pressure of 20,000 lbs. per sq. in. is required for plastic deformation of the crystalline polymer at the same temperature. When the supercooled plastic is stretched at room temperature, the molecules are oriented along the major axis. See Figure 15.12. The rate and

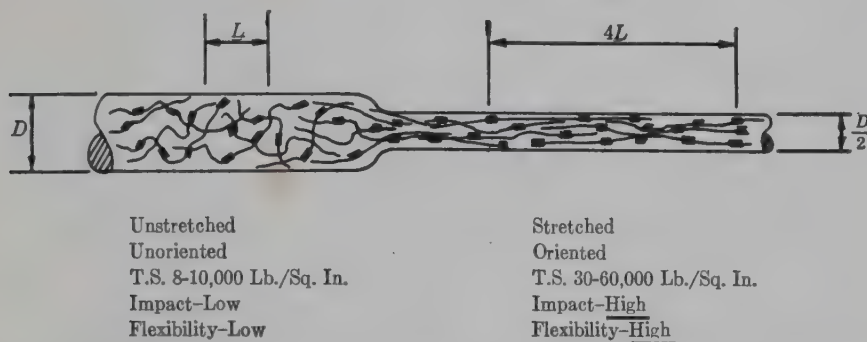


FIG. 15.12. Orientation of molecules of Saran as a result of stretching.
(Goggin and Lowry, *Ind. Eng. Chem.* **34**, 331, 1942.)

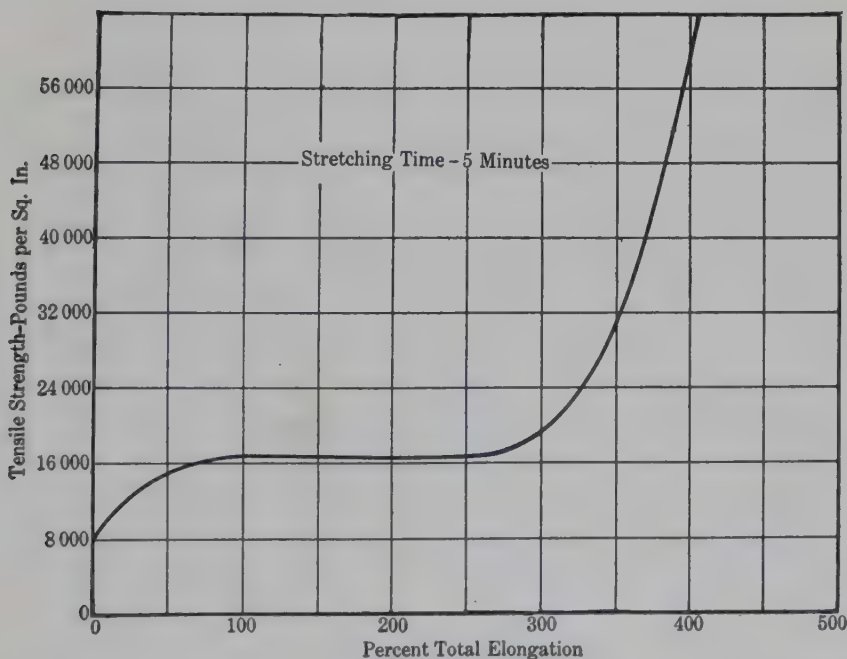


FIG. 15.13. Effect of elongation upon tensile strength of Saran.
(Goggin and Lowry, *Ind. Eng. Chem.* **34**, 331, 1942.)

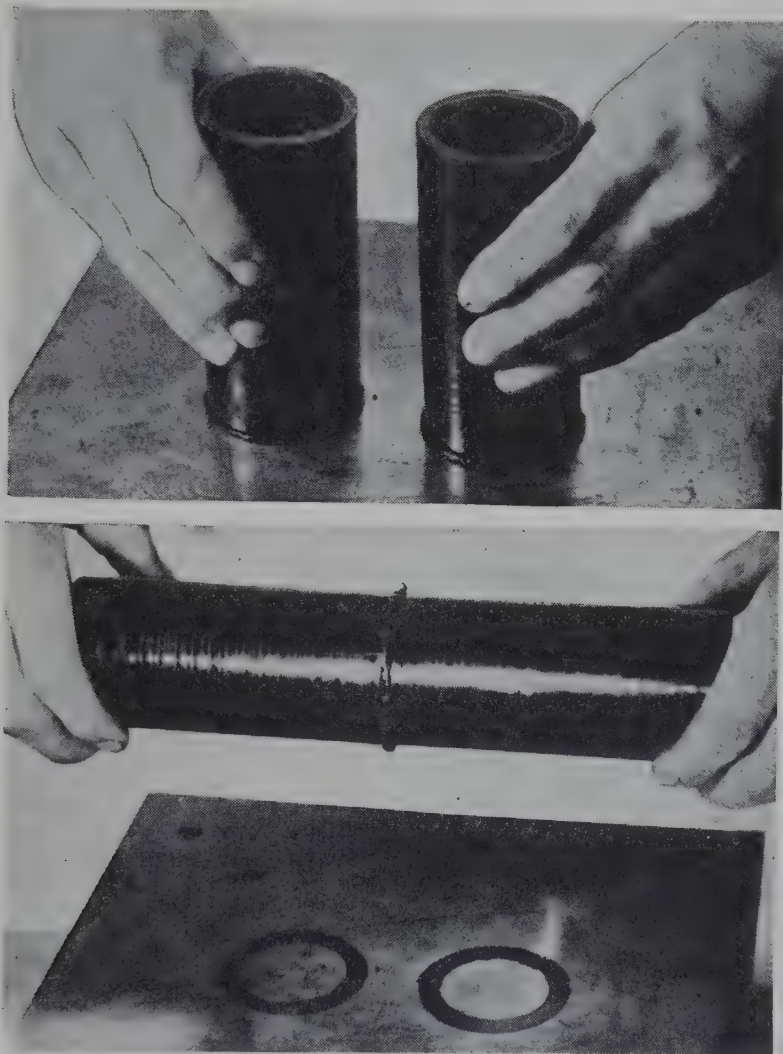
extent of crystallization which occurs will depend upon the regulation of the temperature either during or after the mechanical processing. The tensile strengths of the monofilaments produced depend upon the amount of elongation as shown in Figure 15.13.

Due to the insolubility of polyvinylidene chloride in most organic solvents, it has not been used very much in lacquers and coatings. However, pure polyvinylidene chloride (purified by removing a small amount of acetone-soluble polymer) which has a softening point of 180–190° C., may be dispersed in trichlorobenzene as a solvent by heating the mixture of polymer (25%) and solvent (75%) to 150–160° C., and adding 0.2–2% of sodium stearate as a dispersion assistant. This dispersion can be applied as a wire coating at a temperature of 150–155° C. Copolymers with vinyl chloride which are soluble in dioxan, trichlorobenzene and cyclohexanone form solutions which are suitable as lacquers and coatings.

Properties and Applications.—The essential characteristics of polyvinylidene chloride are similar to those of polyvinyl chloride, though in certain respects the vinylidene polymer is superior to the vinyl polymer. For example, Saran is highly resistant to the action of acids, alkalies (except concentrated ammonium hydroxide), salt solutions and organic solvents, except cyclohexanone and dioxan. Related to this general inertness is the extreme resistance of polyvinylidene chloride to water. The polymer shows no measurable absorption of water after a 24-hour immersion, and hence this plastic is comparable with polystyrene in moisture resistance. This extremely low water absorption accounts for the polymer maintaining dimensional stability under a wide range of moisture-exposure conditions. Other general characteristics such as non-toxicity, lack of odor, non-flammability, excellent aging stability under a wide range of sunlight and humidity conditions, relatively high softening point as compared with other thermoplastics, and colorability further indicate the basic similarity of the polyvinyl and polyvinylidene types.

The principal characteristics for which this plastic type is most noted, however, are concerned with the factors of mechanical strength and ease of fabrication. Excellent values of tensile and flexural strengths, abrasion resistance and impact strength are recorded if the fabrication has been correctly performed. Tensile strength values as high as 50,000 lbs. per sq. in. have been obtained with Saran monofilaments. The flexural strength of a 5/16 in. Saran tubing having a wall thickness of 1/16 in., was found to be very much greater than a standard 1/4 in. copper tubing. The Saran tubing was flexed through a 15° arc, 1750 times per minute for 2,500,000 cycles and was still unruptured. The copper tubing failed after 500 cycles. In the case of extruded Saran tapes, the longitudinal strength is greater than the transverse strength. Both of these

values can be improved by rolling the strip between the rollers of an ordinary rolling mill, gradually decreasing the distance between the rollers. When a test sheet, 4 inches square and having a thickness of 1.035 inches, was rolled until it was approximately 7 inches square and had a thickness of 0.012 inch (this sheet was rotated 90° after



FIGS. 15.14A and B. Welding of Saran pipe. (Courtesy of The Dow Chemical Company.)

each pass between the rollers), its tensile strength increased from 4000 lbs. per sq. in. to 6700 lbs. per sq. in., and its flexural strength increased almost forty-fold.

Extruded Saran rods or tubes may be used for making gaskets, valve seats, ball checks, medicinal probes, chemical resistant flexible

tubing and pipe. Saran pipe can be easily welded by heating the two ends to approximately 177° C. (350° F.), and holding them together for a few seconds. See Figure 15.14A and B. Saran can also be made in the form of corrosion-resistant tape for wrapping joints, chemical conveyor belts, and wearing apparel.

Circular monofilaments with diameters from 0.007 to 0.100 inch, and filaments of other shapes up to 0.200 inch maximum dimension have been made from the oriented crystalline product. These filaments are used to make filter fabrics, special ropes, fishing lines, belts, suspenders, handbags, upholstery fabrics (Figure 15.15) for use on train and bus seats as well as for household furniture and automobile seat covers.

TABLE V-15. COMPARISON OF PHYSICAL PROPERTIES OF POLYMETHYL METHACRYLATE, POLYSTYRENE, POLYVINYL CHLORIDE-ACETATE AND POLYVINYLIDENE CHLORIDE RESINS ^a

	Polymethyl Methacrylate	Polystyrene	Polyvinyl Chloride-Acetate	Polyvinylidene Chloride
Specific gravity	1.18	1.07	1.35	1.70
Refractive index N_d	1.49	1.59	1.53	1.61
Tensile strength, lbs. per sq. in.	5,000-7,000	5,000-9,000	9,000	5,000-7,000
Modulus of elasticity, lbs. per sq. in. $\times 10^6$	6.0	1.7-2.6	3.5-4.1	.8-1.7
Compressive strength, lbs. per sq. in.	10,000-15,000	13,000	11,000	—
Flexural strength, lbs. per sq. in.	9,000-15,000	14,000-19,000	10,000-13,000	16,000
Impact strength, ft. lbs. per in. of notch	.25-.50	.35-.50	.2-1.4	1.0-4.0
Hardness Brinell, 25 kg.	18-25 (500 kg.)	20-30	15-25	—
Thermal conductivity, 10^{-4} cal. per sec. per cm. per ° C.	4.3-6.8	1.9	4.0	2.2
Thermal expansion, $\times 10^{-6}$ in. per in. of length per ° C.	7.0-9.0	6.0-8.0	6.9	15.8
Safe top operating temperature, ° F.	140	155-200	130	160-200
Softening point, ° F.	174-203	190-230	140-150	240-280
Distortion under heat, ° F.	—	170	148-158	150-200
Cold flow	Slight	Slight	Slight	Slight
Dielectric strength, volts per mil	480	500-700	400-500	500
Power factor, 10^6 cycles	.015	.0001	.02-.065	.03-.05
Water absorption, per cent in 168 hrs.	.4	.05 (318 hrs.)	.05-.15	.00 (24 hrs.)
Elongation, per cent	5-15	2-5	3.5-8.5	10-40

^a A Ready Reference for Plastics, 1943 Edition, Boonton Molding Company, Boonton, N. J.



FIG. 15.15. Car seats covered with Saran. (Courtesy of The Dow Chemical Company.)

Injection-molded Saran is used for making spray-gun handles, valve seats, acid dippers, products for the rayon industry, such as spinneret couplings, gasket holders, filter parts, nozzle tips, rollers and guides, shoe soles and heels.

Review Questions

1. Write equations showing how each of the monomeric vinyl compounds, discussed in this chapter, can be prepared.
2. Which vinyl types are prepared by the polymerization of monomers, and which are obtained by modification of a polymer.
3. Indicate the reactions involved in the preparation of polyvinyl butyral from vinyl acetate.
4. What factors are involved in the variations of properties of different types of:
 - (a) Polyvinyl alcohol
 - (b) Polyvinyl chloride-acetate copolymer?
5. Describe one polymerization technique for the preparation of polyvinyl acetate.

6. What vinyl resin would you select for properties of:

- (a) High softening point
- (b) Water solubility
- (c) Flame resistance
- (d) Water resistance
- (e) Solubility in organic solvents
- (f) Adaptability to injection molding or extrusion
- (g) Film strength with high proportions of plasticizer?

7. What vinyl resins would you select to produce:

- (a) Coating for paper
- (b) Safety glass
- (c) Surgical sutures
- (d) Outdoor upholstery
- (e) Oil-resistant gasket
- (f) Vinyon
- (g) Water-resistant fabrics
- (h) Filter cloth
- (i) Emulsifying agent?

8. What is photopolymerization? How is vinyl chloride polymerized by this method?

9. What is the evidence in favor of a 1,3 arrangement of monomeric units in polyvinyl chloride?

10. When is a heat stabilizer used as a compounding agent?

11. How may a thermosetting type of polyvinyl butyral be compounded? By means of formulas show the cross-linking involved in the cure.

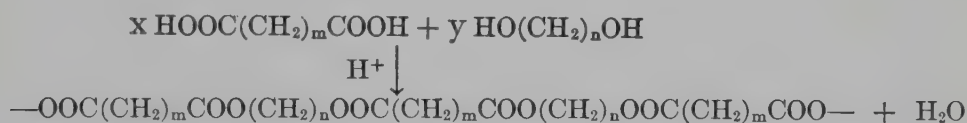
12. What is the importance of copolymerization in the polyvinylidene chloride class of resins?

13. What is the relationship of: (a) amorphous, (b) crystalline, (c) oriented crystalline, states of polyvinylidene chloride? How may each be produced?

CHAPTER XVI

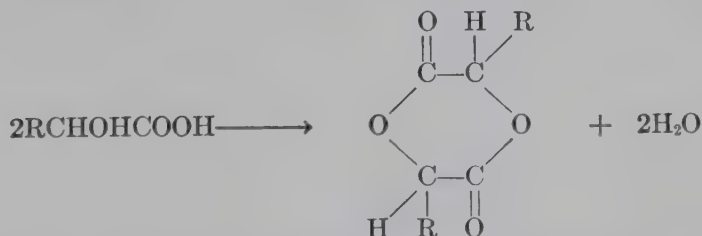
SYNTHETIC PLASTICS VII: ALKYD RESINS: THERMOPLASTIC AND THERMOSETTING

The alkyd group of resins consists of numerous polyesters usually obtained from a polycondensation reaction between polyhydroxy alcohols and polycarboxylic acids, or from a polymeric inter-esterification of hydroxy acids. Since these resins are usually prepared by an esterification reaction, the following general equation represents their formation,

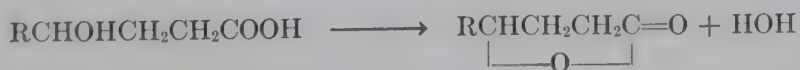


This reaction illustrates the growth of a linear polymer by the interaction of molecules which contain two functional groups. The nature of the terminal groups depends upon the relative number of moles of acid and alcohol used. If the acid is used in excess, the majority of terminal groups will be carboxyl; if the alcohol is used in excess, the majority of terminal groups will be hydroxyl. When a dicarboxylic acid and a dihydroxy alcohol are used, the polymer formed is a linear, thermoplastic resin.

Linear thermoplastic resins can also be made by the inter-esterification of ω -hydroxy acids of the type $\text{HO}(\text{CH}_2)_n\text{COOH}$, where $n = 5-20$. In the case of low molecular weight hydroxy acids there is a possibility that cyclic lactides or lactones will be formed. α -Hydroxy acids generally yield lactides when heated, e.g.,

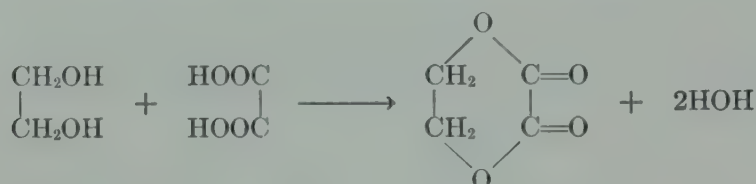


β -Hydroxy acids lose water when heated, forming α , β -unsaturated acids, while γ - and δ -hydroxy acids yield lactones, e.g.,



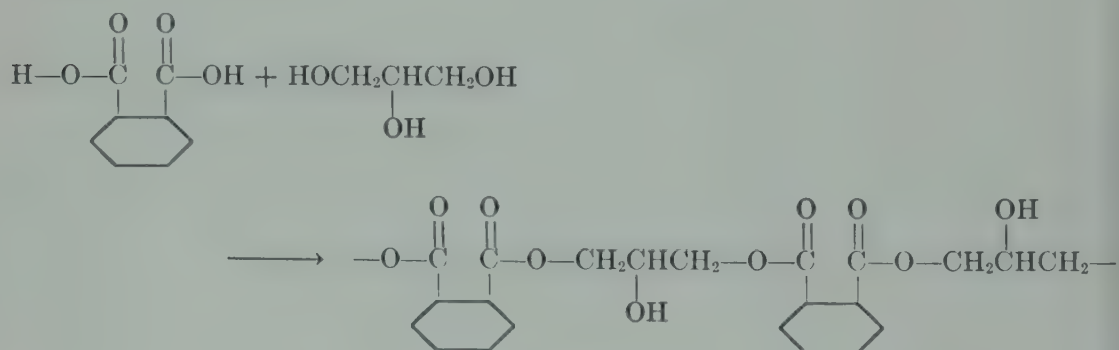
The most common lactides and lactones are those containing five- and six-membered rings. If the hydroxyl and carboxyl groups are so spaced that cyclization would involve the formation of larger rings, linear polymers are the principal or only products obtained. (See p. 31.)

Cyclization is not an important factor when considering the interaction of polyhydroxy alcohols and polycarboxylic acids, because the only combination of these two types which yields a six-membered ring is that of ethylene glycol and oxalic acid, e.g.,

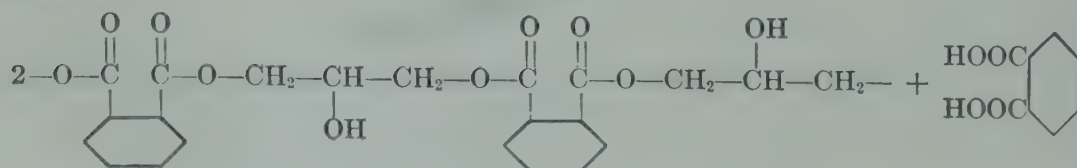


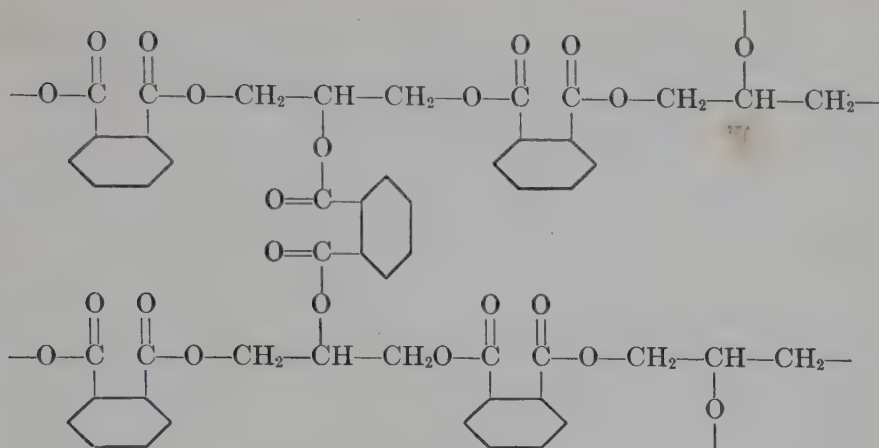
Of greater importance in the field of industrial plastics, however, are the cross-linked or net polymers which result when a component with three functional groups is chosen. Thus, when glycerol replaces the dihydroxy alcohol in the above reaction, the chemical change which results when heat is applied may be represented as occurring in two stages:

Stage I



Stage II





In the first stage, a normal chain growth proceeds by reaction of the terminal hydroxyl groups of glycerol (i.e., α -esterification) with the dicarboxylic acid present. When approximately one-third of the free acid remains in the reaction vessel, or when the rate of the linear esterification reaction decreases sufficiently, β -esterification may proceed with a rapid decrease of the acid content and production of the resin in the gelled or insoluble state. During the latter process, the far-reaching effects of a slight degree of esterification are noticeable by the rapidity with which the molecular weight increases and the solubility and fusibility decrease as the cross-linkage reaction occurs. This second stage proceeds to an extent which is dependent upon the amount of acid present, for it has been found that the greater the amount of dicarboxylic acid present, the greater will be the insolubility and infusibility of the resultant product. An approximate molecular weight of 2000 has been estimated for the insoluble, cross-linked polymer obtained just prior to gelation.

The actual mechanism of the condensation to a polymer is simple for it involves only an esterification reaction of the alcohol and acid (or anhydride). Thus, the components may be allowed to react directly, with suitable control of the temperature, until the desired stage of gelation has been reached. Although a high-boiling solvent may be used to dilute the reaction mixture and thus facilitate the control, most processes employ a mass reaction. Control is effectively carried out in most cases by regulation of the acid (sulfurous, hydrochloric, aromatic sulfonic, formic or acetic acid) used as the catalyst. Other convenient agents utilized in regulating the hard-

ening of the resin include metallic soaps, calcium oxide, boron trifluoride, zinc oxide, or acid chlorides. Retardation of the process is effected by naphthalene, urea or thiourea.

The versatility of the alkyd resins is responsible for their industrial popularity. Although the use of such types in resin applications was first noted by Watson Smith in 1901, the industrial growth did not become significant until 1926 when phthalic acid became available in commercial quantities, as a result of its formation by the catalytic oxidation of naphthalene. The first alkyds were known as Glyptals, and were made from phthalic acid and glycerol. The growth and development of these polyesters, however, has been achieved as a result of the introduction of new and valuable properties by varying the composition of the acid and alcohol used and by the addition of modifying agents such as drying and non-drying oils, fatty acids, and natural or synthetic resins. For example, two interesting and useful types of alkyd resins are obtained (1) by the use of a monobasic acid, either saturated or unsaturated, in addition to the dicarboxylic acid necessary for polycondensation, or (2) the addition of a natural resin, e.g., rosin, which contains a carboxyl group. The essential types of alkyd resins may be summarized as follows:

1. *Non-convertible.* These are thermoplastic resins which cannot be converted by heat into an insoluble, infusible form.

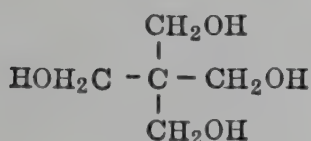
2. *Heat-convertible.* These contain a sufficient number of functional groups to permit the formation of a cross-linked polymer.

3. *Element Convertible.* These resins are obtained when unsaturated acid radicals are introduced into the resin molecules, and are capable of being changed on oxidation to a hard, cross-linked form.

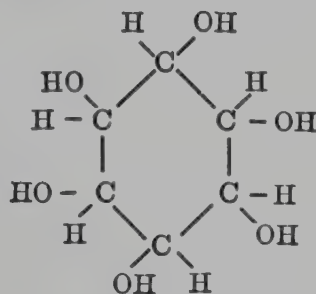
Variation of Properties with Different Acids and Alcohols.—As mentioned previously, the most important properties variation is that thermoplastic polymers are obtained as a result of a bi-bifunctional reaction and thermosetting polymers are obtained when a bi-trifunctional or higher functional reaction occurs (see p. 27). The thermoplastic resins may be soft and rubber-like (e.g., polymer from diethylene glycol and sebacic acid), and the thermosetting resins may be hard and brittle (e.g., polymer from glycerol and phthalic anhydride). An increase in the length of the polymethylene chain of either the acid or the alcohol causes

1. an increase in the solubility of the polymer in organic solvents¹;
2. a decrease in water solubility;
3. an increase in the viscosity of the molten polymer;
4. a greater tendency to form a high molecular weight polymer;
5. a greater tendency to form fibrous products.

In addition to using dihydroxy and trihydroxy alcohols, it is possible to use polyhydroxy alcohols such as pentaerythritol (A) and hexahydroxycyclohexane (inositol) (B).



A



B

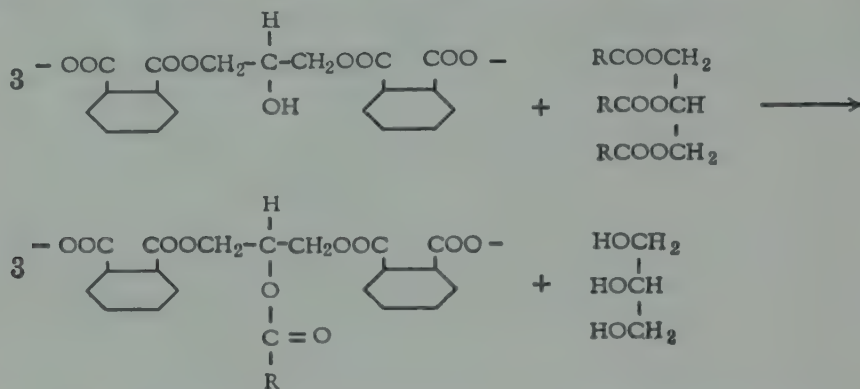
Polymers obtained from the interaction of these alcohols with dicarboxylic acids have numerous cross-linkages and consequently are hard and brittle.

Polymers obtained by the interaction of dicarboxylic acids with mixtures of dihydroxy and monohydroxy alcohols are soft and have been found useful in making coatings.

Addition of Monobasic Acids.—A monobasic acid may be added for the purpose of further adjusting the properties of the final product. Since this type of acid contains only one carboxyl group, it will not aid in the formation of a polymer. When a saturated monobasic acid is used alone with a polyhydroxy alcohol, no polymerization occurs and the product is a high-boiling ester which may be of value as a plasticizing agent. If a mixture of monobasic and dibasic acids is used, the monobasic acid will tend to block the growth of the polymer by reacting with the available hydroxyl groups. In this case, low molecular weight polymers will be produced. The presence of a monobasic acid also tends to eliminate cross-linking. However, if the monobasic acid is unsaturated and capable of combining with other unsaturated linkages, polymer growth and cross-linkings may occur by an addition type of reaction rather than by esterification. Suitable unsaturated monobasic acids for this purpose may be

¹ The unmodified alkyds are readily soluble in chlorinated hydrocarbons and esters but are practically insoluble in hydrocarbons of either the aliphatic or aromatic type. Higher alcohols may be used as diluents when decreased viscosity is desired.

produced by the hydrolysis of semi-drying and drying oils. The acids, consequently, may be designated by the same terms. It is not necessary to isolate the acid, for good results are obtained by using a naturally occurring glyceryl ester of the desired type of acid. In this case, the reaction of the glyceryl ester with the linear polymer is an ester interchange, rather than esterification, e.g.,



If the acid which is introduced either by direct esterification or ester interchange is saturated, or is unsaturated but of such a nature that polymerization is negligible even over a long period of time, the resulting product is classed as a non-drying alkyd resin. The semi-drying alkyd resins are made from moderately unsaturated acids and harden when baked at elevated temperatures. When highly unsaturated acids are employed, the product is known as a drying alkyd resin. These resins harden rapidly when baked or more slowly when exposed to air. The essential difference between the semi-drying and the drying alkyd resins is that the latter polymerize and harden more rapidly than the former, under the same conditions.

Non-Drying Alkyd Resins.—For the manufacture of a non-drying alkyd resin, the saturated fatty acid or the relatively saturated naturally-occurring glyceryl ester usually comprises 25–40% of the total charge, the remainder being the polyhydroxy alcohol (usually glycerol) and the dicarboxylic acid. Stearic, palmitic and lauric acids can be used, while cocoanut oil (iodine number ² 6–10), castor oil (iodine number 84) and cottonseed oil (iodine number 103–111) are typical of the naturally-occurring oils used.

This type of resin is characterized by increased softness and flexibility when compared with other alkyd resins. It has proved extremely valuable as a modifying and plasticizing agent in lacquers made from cellulose nitrate, ethyl cellulose and drying alkyd resins.

² Iodine number is the number of grams of iodine which will add to 100 grams of the oil and is an indication of the amount of unsaturation of the oil. A low iodine number indicates very little unsaturation.

A mixture of approximately equal parts of cellulose nitrate and non-drying alkyd resin together with about 10% of plasticizer dissolved in a suitable mixture of solvents is an excellent lacquer. When compared with the older cellulose nitrate lacquers, it is found to possess improved adhesion, flexibility and toughness, less tendency to chalk and better retention of color. Similar effects are noted in enamel finishes made from mixtures of non-drying and drying alkyd resins.

Semi-Drying and Drying Alkyd Resins.—The most important application of the alkyd resins is their use for protective coatings of all types. The addition of drying oils to a resin formulation permits variation of both film characteristics and the technique of application and hardening. A non-alkyd oil varnish such as those produced from linseed or tung oil requires a long period to dry, but the drying-oil alkyds dry rapidly without loss of the adhesion and film strength associated with the former. The drying reaction is an oxidation process, accompanied by polymerization, and is catalyzed by the addition of various water-insoluble metallic soaps of lead, cobalt and manganese. These are known as “driers.” Combination of the drying oil or acid with the glyceryl phthalate, maleate or sebacate results from mixing the oil and resin in a high-boiling solvent during the esterification reaction. Typical oils which may be used include dehydrated castor, linseed (iodine number 175–202), China wood (iodine number 190–197), soya (iodine number 122–134), sunflower (iodine number 129–136), and hempseed (iodine number 141). The degree of combination is determined by the relative proportions of oil to resin. The ratio of ingredients is expressed by the *oil lengths* of the resultant products. These are shown in the following table:

TABLE-16 ^a

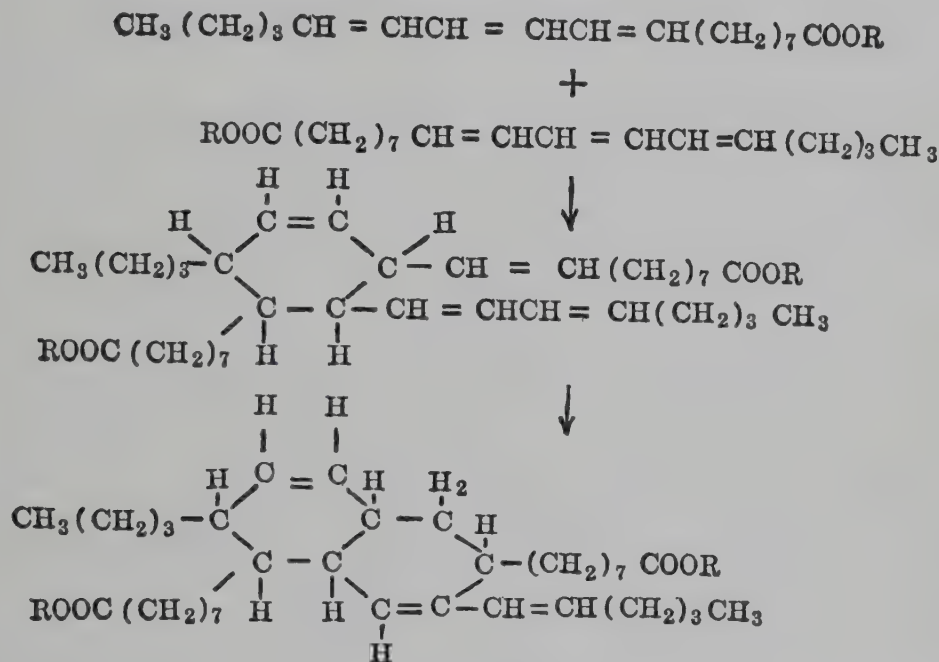
Per Cent Glyceryl Phthalate Resin		Per Cent Oil-Acid
Short oil	60–70	30–40
Medium oil	50–60	40–50
Long oil	33–50	50–66

^a Simonds & Ellis, *Handbook of Plastics*, p. 442, Van Nostrand Co., New York, 1943.

Solubility of the resin varies as the oil length increases. Greater compatibility with petroleum thinners, and, therefore, reduced costs, result from greater proportions of oil or acid. Long oil resins are generally used for exterior applications while medium and short oil resins are used principally for interior applications. When completely cured, either by baking or as a result of slow oxidation and

A closely related theory is that the formation of a peroxide gives rise to a polar group in the molecule and that a cross-linkage is virtually formed by the association of two such polar constituents.

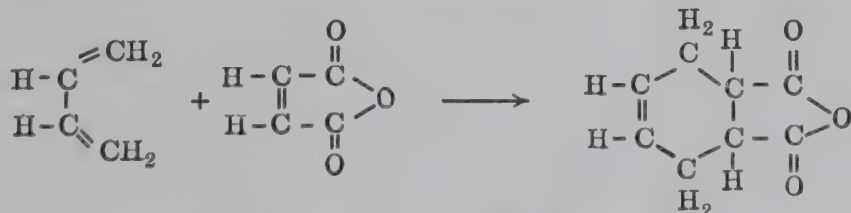
Another hypothesis is that the drying oil residues may interact with each other to form a bicyclic ring system resulting in mutual saturation of some of the double bonds. The first step in this polymerization may involve a diene synthesis ³ (Diels-Alder reaction), which may be followed by or accompanied by a second ring closure to form a bicyclic ring system, e.g.,



In these formulas, R represents a linear polymeric alkyd chain. This general type of structure has been proposed by Bradley and Johnston ⁴ for the dimers of methyl and ethyl eleostearates.

A similar mechanism has been proposed by the same authors for the dimerization of methyl and ethyl linoleates. Since linoleic acid,

³ A simple example of the diene synthesis is the reaction of 1,3-butadiene with maleic anhydride,

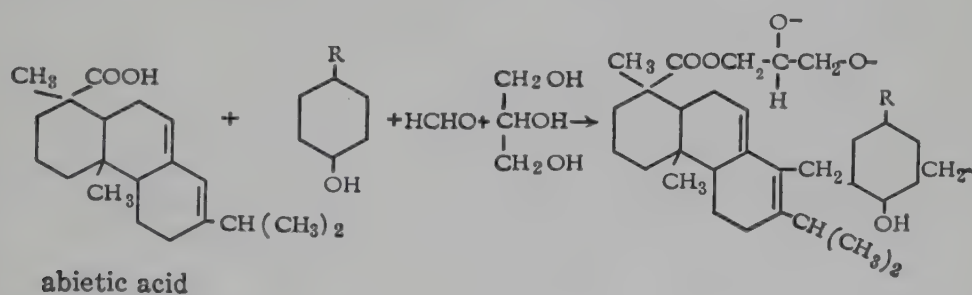


⁴ Bradley and Johnston, *Ind. Eng. Chem.* **32**, 806 (1940).

A reaction which is similar to the drying reaction of varnishes is the formation of *factice* by saturation of the double bonds of oils by either sulfur or sulfur monochloride (S_2Cl_2). The analogy with the vulcanization of rubber will be noted.

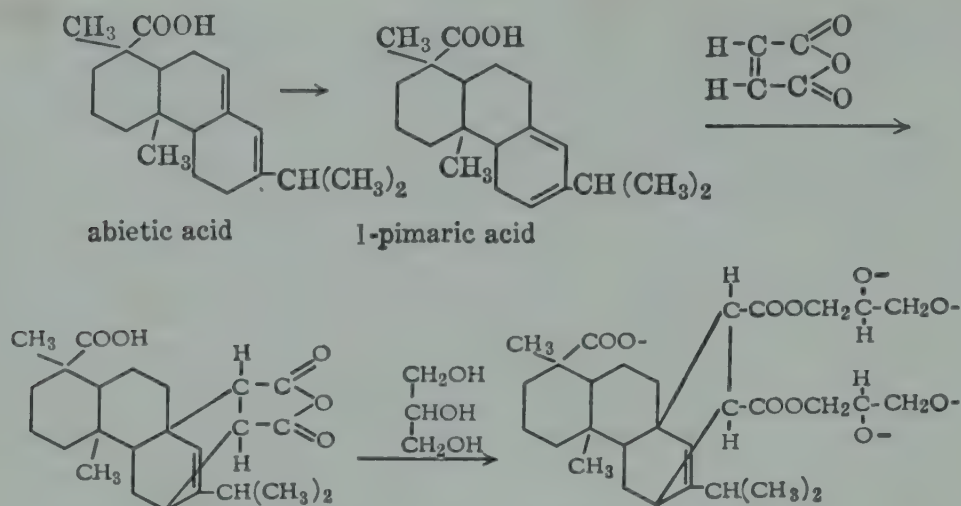
Addition of Natural Resins.—Modification of alkyd resins by the incorporation of natural resins such as rosin or copals and, in some cases, addition of reactive thermosetting types such as phenol-formaldehyde or urea-formaldehyde is useful in adjusting the alkyd properties for specific applications. Generally, the addition of resin hardens the film obtained from the alkyd, but by the use of oils in conjunction with the resins, numerous degrees of hardness are possible.

The natural resin, if it contains a reactive functional group, such as a carboxyl group, may be used directly in the esterification reaction, along with the dicarboxylic acid and the polyhydroxy alcohol. The resin may also be allowed to react with phenol and formaldehyde to form a condensation product which is capable of reacting with glycerol or some other polyhydroxy compound. The formation of such a product is illustrated by the phenolic residue incorporated into Amberol and Beckacite.



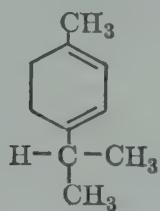
A type of adduct which is of considerable importance in the manufacture of alkyd resins is that formed by the diene synthesis. In this way, numerous dibasic acid anhydrides can be formed and subsequently allowed to react with glycerol or some other polyhydroxy alcohol.

A complex example of the use of the diene synthesis is the reaction between rosin (essentially abietic acid) and maleic anhydride. This reaction occurs only at temperatures above 100° C., and since the product is identical with that obtained from *l*-pimaric acid and maleic anhydride at lower temperatures, it is assumed that abietic acid first isomerizes to form *l*-pimaric acid.

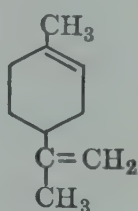


Polymers similar to this are known as Amberols, Beckacites and Maleics.

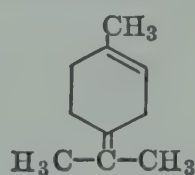
Monocyclic terpenes, e.g., α -terpinene, which have a conjugated system of double bonds will add to maleic anhydride to form a Diels-Alder adduct. Monocyclic terpenes, e.g., limonene and terpinolene, which do not have a conjugated system of double bonds will isomerize to α -terpinene if any acid, even maleic acid, is present, and will then add to maleic anhydride in the usual way. The formulas for α -terpinene, limonene and terpinolene are given below.



α -terpinene

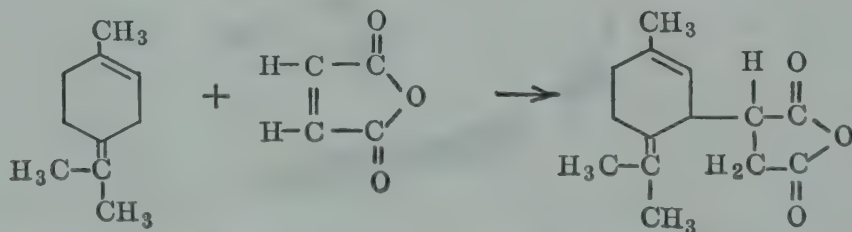


limonene



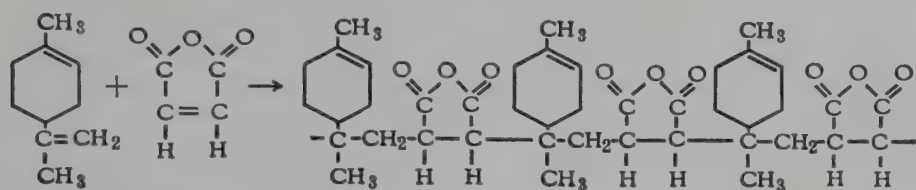
terpinolene

However, if a terpene such as limonene or terpinolene is allowed to react with maleic anhydride in the absence of maleic or any other acid, a different reaction occurs.⁶ Approximately one-half of the terpene adds to maleic anhydride as follows:



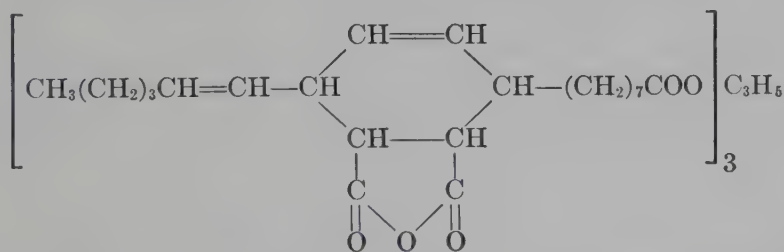
⁶ Ensor and Little, Pittsburgh Meeting, *Am. Chem. Soc.*, Sept. 1943.

The other half of the terpene combines with maleic anhydride to form an addition type of copolymer, e.g.,



The combination of Diels-Alder adduct and addition copolymer is marketed as Petrex Acid. The Diels-Alder adduct will react with a dihydroxy alcohol to form a linear polyester. The addition polymer will react with a dihydroxy alcohol to form a cross-linked polymer. In the mixed polymer, the linear polymer would act as a plasticizer for the cross-linked polymer. By varying the number of atoms between the two hydroxyl groups of the dihydroxy alcohol, it is possible to get products varying from hard, brittle resins to fluid, non-gelling resins. A monohydroxy alcohol yields a high-boiling liquid, suitable for use as a plasticizer, and glycerol yields a hard, brittle resin which is very soluble in alcohol and has been used extensively as a substitute for shellac.

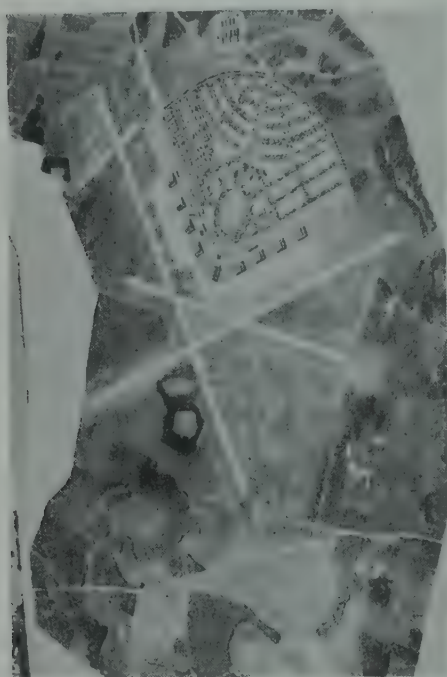
Yet another example is that involving the interaction of tung oil with maleic anhydride:



From these examples, it can be seen that a wide variety of acid anhydrides can be obtained from naturally occurring unsaturated compounds by reactions with maleic anhydride. These, in turn, give rise to the formation of numerous alkyd resins having varying properties.

General Properties.—Each of the resin types referred to above may be supplied in solid, solution, or emulsion form. Since most of the practical importance of the alkyds depends upon their use as protective coatings, it is not surprising to find the compounding data dealing chiefly with solutions and emulsions. Since the actual data for each resinous form will depend upon the chemical type involved, no general rules of solubility or practical adaptation with

modifying agents may be outlined. The fundamental rule of solubility suggests the use of oxygenated solvents, and the importance of cellulose derivatives in the coating industry suggests the use of alkyds in conjunction with such a film-forming material as cellulose nitrate.



A (before)



B (after)

FIG. 16.1. Airfield before and after camouflaging with paint made from alkyd resins in emulsion form. (Courtesy of Resinous Products and Chemical Company.)

As mentioned previously, the properties of the base resin are easily modified by varying the nature and the amounts of the acid and alcohol used. General factors such as good wear resistance, durability of finish, adaptability of solubilities and compatibilities, fair film-strength, high gloss, and excellent adhesion are characteristics usually associated with the alkyds.

Applications and Trade Names.—The resins of the alkyd class may be applied as enamels, lacquers, textile finishes, metal primers, caulking compounds, slushing mixtures, protective films, leather coatings and water-emulsion paints. The products may be applied by spraying, brushing, dipping, hot melt or knife spreading. Applications outside of the coating industry include the use of alkyds as gaskets, printers' rolls, flexible insulation, and as binders for mica and pigments. Drying oil modified alkyd resins can be used as vehicles

for pigments such as carbon black and monastral blue. The pigmented resin is emulsified usually to form a water-in-oil type of emulsion and the emulsion is used for the coloring of textiles.

The trade names indicate the heterogeneous forms which may be produced in this class. The list includes: Amberlac, Aquaplex emulsions, Arochem, Aroplaz, Beckacite, Beckasol, Dulux, Duraplex, Dyal, Dynal, Esterol, Falkaloid, Falkyd, Glyptal, Makalot Alkyd, Mirasol, Paraplex, Pentalyn, Petrex, Rauzone, Rezyl, Syntex and Teglac.

Review Questions

1. By means of formulas, show why some alkyds are thermosetting while others are thermoplastic.
2. What methods are used in order to vary the properties of the alkyds?
3. What is the chemical difference between non-drying and drying types of modified alkyds? Illustrate.
4. What advantages result from the use of an unsaturated acid or ester in the preparation of an alkyd?
5. What is the importance of the Diene reaction? Illustrate by showing the reaction between abietic acid and maleic anhydride followed by the reaction with glycerol.

CHAPTER XVII

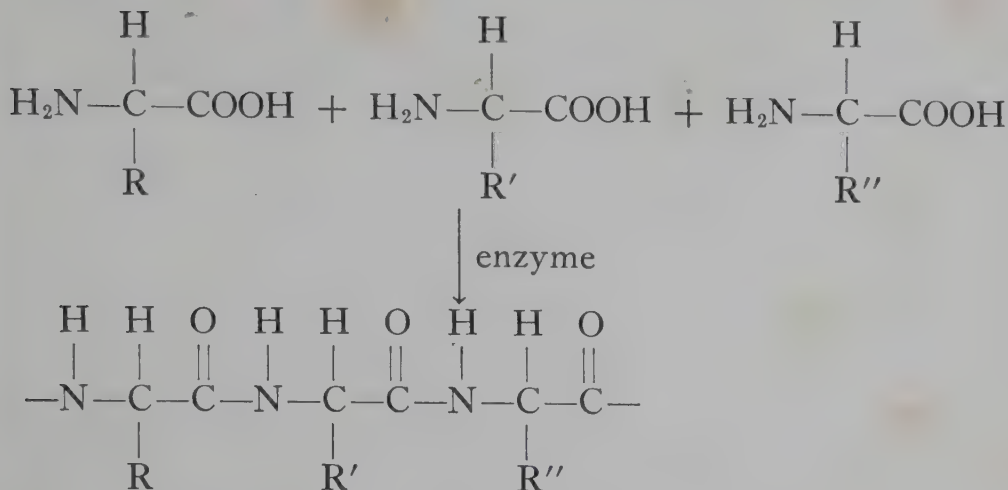
SYNTHETIC PLASTICS VIII: THE PROTEIN PLASTICS

The class of protein plastics consists of those naturally occurring protein materials which may be adapted by various methods to plastics applications, and also true synthetic materials which approach a protein structure in their chemical composition. Nylon is an example of the latter type.

CASEIN PLASTICS

The first appearance of the use of protein material for plastics applications was in 1897 when Krische and Spitteler showed that casein could be hardened by immersion in a formaldehyde bath. At that time celluloid was the only synthetic plastic available for commercial use. Interest was shown in the casein product, therefore, because of its advantage over cellulose nitrate in flame resistance. Commercial development of the plastic in this country was not started, however, until about 1920. From the beginning, inherent weaknesses in the properties of Galalith, as it was then called, limited the use of casein plastics to a few simple products requiring no great strength and weatherability. Although improvements have been introduced in the fabrication methods and physical properties, the weaknesses have never been eliminated. In later years, casein has grown in popularity because of its consumption in the production of a wool-like fiber. Approximately 200 million pounds of skim milk were used in this country for that purpose in 1941. Skim milk contains about 3% of casein.

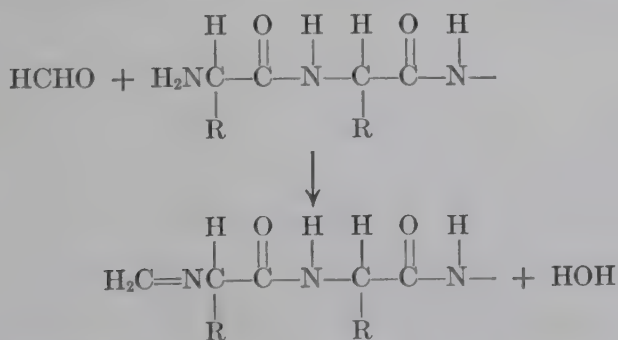
Composition and Hardening of Casein.—Proteins are complex polyamides which are formed, in plants and animals, from amino acids. Since all of the amino acids which have been obtained by the hydrolysis of proteins are alpha amino acids, their synthesis, in plants and animals may be represented as follows:



Seventeen different amino acids have been isolated from the hydrolysis products of casein, which has a molecular weight of 375,000, determined by means of the ultracentrifuge. In addition, the hydrolysis of casein also yields a phosphoric acid derivative known as a nucleic acid. Consequently, casein is classed as a phosphoprotein or nucleoprotein.

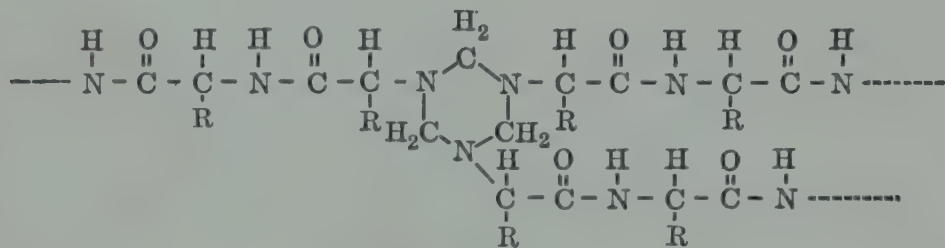
Although some proteins, such as keratin (in horn and wool) and fibroin (in silk) are known to have a fibrous chain, casein has a completely amorphous structure and is probably somewhat globular in shape. It is of interest, also, to note that casein contains about 5.5% of its nitrogen content in the form of primary amine groups, $-\text{NH}_2$. Originally this led to the postulate that the hardening action of formaldehyde resulted from the formation of $-\text{N}=\text{CH}_2$ groups. Later research has indicated, however, that cross linkages are formed between polymeric chains as the hardening proceeds.

The chemical reactions involved in the hardening of casein plastics with formaldehyde have been the subject of considerable discussion.¹ Since one end of a peptide chain probably contains a primary amine group, it may react with formaldehyde as follows:



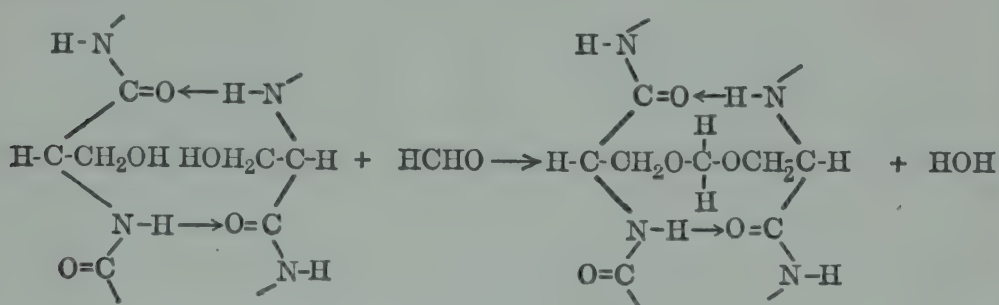
¹ Carpenter and Lovelace, *Ind. Eng. Chem.* **34**, 759 (1942).

Three such modified peptide chains could polymerize in the same manner as other $\text{H}_2\text{C}=\text{NR}$ compounds to form a substituted hexahydro-sym-triazine, e.g.,



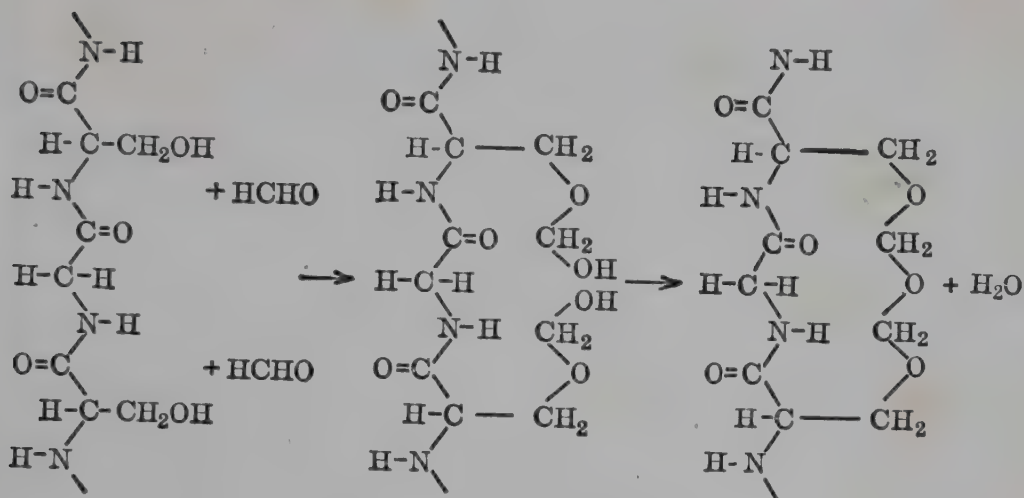
It is also possible for this same type of trimer to be formed from methylene amino groups resulting from the interaction of formaldehyde and primary amine groups present in side chains of the peptide chain.

However, Carpenter and Lovelace found that casein (precipitated by acetic acid) reacted with more than the calculated amount of formaldehyde, assuming that the molecular weight of the casein was 100,000 and that not more than one molecule of formaldehyde would react with each amino acid residue. This indicates that some other kind of reaction occurs between casein and formaldehyde. These investigators suggested three other possible methods by which formaldehyde could react with the peptide chains to produce hardening effects. Acid casein contains 8.96% of amino acid residues which contain hydroxyl groups on the β -carbon atoms. Consequently two peptide chains could be cross-linked by means of an acetal type of linkage, e.g.,

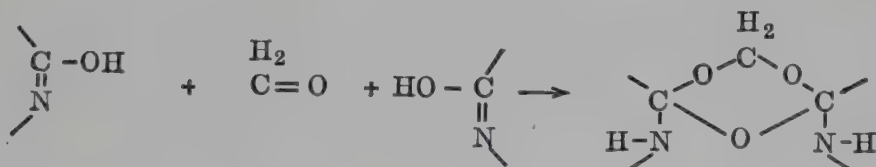


This type of reaction would not only increase the molecular weights of the units present in the hardened plastic, but it would also destroy the hydroxyl groups and hence would improve the resistance of the plastic to water.

A second method of eliminating hydroxyl groups is by the interaction of two hemiacetal groups formed from alternate β -hydroxy amino acid residues in a peptide chain.



The third mechanism proposed by Carpenter and Lovelace does not involve the hydroxyl groups present in the molecule. They assume that the peptide linkage may exist in the tautomeric enol form and that two such linkages on adjacent chains could react with formaldehyde to form a substituted trioxymethylene ring.



Since this mechanism involves only the peptide linkage it would apply to any adjacent peptide chains, regardless of whether or not they contained any hydroxy amino acid residues.

Manufacture and Fabrication.—The manufacturing and fabrication processes for casein plastics may be summarized as follows:

(a) The 3% casein present in skim milk is precipitated by the enzyme, rennet.

(b) The separated casein is washed, filtered and ground into a powder after drying.

(c) The dried powder is then mixed thoroughly with various compounding agents such as talc, benzanilide, tricresyl phosphate, glycerol, triethanolamine, metallic carbonates and volatile organic solvents. Water is also added to soften the casein during the kneading process, though the addition of too much water will cause

the formation of a soft plastic which will shrink considerably when dried. Alum is also added at this point in order to provide sufficient hardness for the plastic to be machined before the final curing or hardening.

(d) The kneaded mass may be formed into rods or tubes by means of a hot extrusion machine. Sheets may be formed by compressing the plastic in a hydraulic press.

At this point, the processing may be modified so as to produce hardening before machining or vice versa. Since the hardening process may require any period of time from one week to six months or a year, depending on the size of the product being processed, it is advantageous to machine into the final form before hardening. An additional reason for machining the object first is that the plastic material which is machined off can be re-used, whereas the hardened plastic scraps cannot be used again.

Thus, it is found more convenient in the production of such materials as buttons and buckles to punch the desired form from the unhardened sheet or rod. The scrap material can then be used again and the hardening process takes place more rapidly. Final hardening occurs as a result of a chemical reaction induced by dipping the product into a formaldehyde bath (4–6% formaldehyde) for the required period of time.

Moisture and excess formaldehyde are removed from the plastic by heating in a sufficiently humid atmosphere so that the outer surface of the plastic does not become hard before the inner portion has had time to dry out. The final step in the processing is one of polishing by machine or treatment with a sodium hypochlorite solution at 65° C. A glossy surface which is superior to a buffed finish is produced in the latter case.

Casein Fiber.—Much progress has been made in the development of a casein fiber which is particularly useful in combination with wool or in felting processes. Essentially the process consists of extrusion of a partially hydrolyzed solution of casein in sodium hydroxide through tiny orifices into an acidic coagulating bath.² The casein used for this purpose is obtained from skim milk by the addition of either sulfuric acid or lactic acid. The precipitated casein is mashed and allowed to soak for thirty minutes in about half the total amount of water to be used. The mixture is heated to 50° C., and enough 8% sodium hydroxide solution is then added to dissolve all of the casein. The mixture is stirred to form a uniform

² Whittier and Gould, *Ind. Eng. Chem.* **32**, 906 (1940).

colloidal solution. One per cent of a flexibilizing agent such as oleic acid, linseed oil acids, glycol phthalate or urea is added, with vigorous stirring. Strengthening agents such as sodium aluminate or calcium hydroxide³ (about 0.8% of total solution) are added to the remaining half of the water at 50° C. The total amount of water should be such that a 10% solution of the casein is formed. The two aqueous solutions are mixed and a uniform mixture is obtained by stirring. The resulting solution is de-aerated by allowing it to stand under vacuum for several hours. During this time the casein undergoes a partial hydrolysis or ripening. It is believed that the hydrolysis consists chiefly in splitting off the side chains, thus decreasing the globular characteristics of the protein molecule so that it will assume a linear configuration when it is reprecipitated.

The de-aerated and ripened solution is forced under pressure through tiny orifices into an acid coagulating bath. A satisfactory coagulating bath consists of an aqueous solution containing 2% sulfuric acid, 5% formaldehyde and 20% glucose. The function of the sulfuric acid is to precipitate the casein from the sodium caseinate solution; formaldehyde acts as a hardening and insolubilizing agent, while glucose has been found most satisfactory in increasing the speed of dehydration of the fiber. The casein is coagulated under slight tension in order to yield a stronger fiber. The fiber is wound on a bobbin and can be further hardened by immersing it in a 5% solution of formaldehyde for sixteen hours. Subsequent treatment with a 5% oil-in-water emulsion of oils used for softening rayon improves the softness and flexibility of the fiber.

An improved method of hardening the casein fibers consists in treating them with ketene⁴ in the presence of a fatty acid acting as a catalyst. This reaction is carried out with partially dried (10–20% moisture content) casein at a temperature of 80–110° C., and from 3 to 15% of ketene is absorbed by the fiber. The improvement in water resistance and the changes in the dyeing characteristics suggest that the ketene has reacted with carboxyl, hydroxyl and amino groups present in the protein molecule. The tensile strength of the ketenized fiber is increased by treatment with a sulfur-containing compound, preferably thioglycollic acid. Although most of the common plasticizers can be used with these ketenized casein fibers, lanolin is preferred. It is also claimed that the ketenized casein fiber,

³ When calcium or barium compounds are used as strengthening agents, from 1–2% of a detergent such as sodium lauryl sulfate is used to prevent precipitation of calcium or barium caseinate.

⁴ Atlantic Research Associates, Brit. Patent 536,841 (1941).

adjusted to a pH of 6–8, will dye substantially the same as wool, so that mixtures of casein and wool can be dyed to the same shade.

Properties and Applications.—The fundamental characteristics of a casein plastic are greatly inferior to those of the more commonly used plastics. Casein products are easily colored in a wide range of possibilities. Likewise, they are easily polished and processed, but the surface gloss is lost when in contact with water. The latter factor is evidence of the extremely poor water resistance characteristic of casein plastics. Samples are encountered which absorb as high as 10% of their weight when immersed in water. As a consequence, the casein products are also characterized by very poor dimensional stability and lack of adequate electrical resistance. There is some evidence that the poor water resistance may be improved by treating the casein with ethyl sulfate or alkylene oxides. The combination of poor properties has eliminated casein from many applications. Buttons, buckles and such novelties now account for its principal uses.

Casein fiber is used as a substitute for wool, especially in the making of felts. The physical properties of wool, casein fiber and soybean fiber are shown in Table I-17. The molded casein plastic is sold by the trade names Ameroid, Gala and Galorn, while casein fiber is known as Aralac.

TABLE I-17. PHYSICAL PROPERTIES OF PROTEIN FIBERS ^a
Tensile Strength, grams/denier, 60% Relative Humidity and 70° F.

Sample	Bundle Test *		Dynamometer Test †		Denier per Filament
	Dry	Wet	Dry	Wet	
Wool	1.07	0.71	1.29	1.02	3.89
Casein	0.87	0.21	0.75	0.26	3.19
Soybean Fiber	0.73	0.15	0.75	0.36	3.03

* Involves combing out sample of staple fiber, placing a known number of fibers in parallel arrangement, taping the ends, and measuring strength of resultant bundle.

† Single fibers with Richards Dynamometer.

^a Simonds and Ellis, *Handbook of Plastics*, p. 367, D. Van Nostrand Co., 1943.

SOYBEAN

Protein plastics derived from this source are mainly used as extenders in phenolic molding powders. Addition of 5–8% causes no detrimental effect and, on the contrary, is claimed to impart

improved strength and hardness. Soybean fibers are made by essentially the same method as that used for casein fibers. The crushed soybeans are freed from oil by extraction with hexane. The remaining soybean meal is dissolved in a 0.1% solution of sodium sulfite and the protein solution is clarified by filtering or centrifuging. The protein is then precipitated from the clear filtrate by the addition of acid, washed and dried. It is dissolved in sodium hydroxide solution, the solution de-aerated, ripened, spun and the filaments hardened as in the case of casein fibers. It is interesting to note that soybean spinning solutions have been obtained which contain 20% of dissolved protein. This more concentrated solution is claimed to have excellent spinning characteristics.⁵

Soybean fibers can be blended with wool in the manufacture of suitings, upholstery fabrics and felts. Their use with cotton and spun rayon has been suggested. See Table I-17, p. 336 for a comparison of the tensile strengths of soybean, casein and wool fibers.

ZEIN

Zein, or corn protein, is extracted from corn meal with isopropyl alcohol. The impurities present, oils and pigments, are removed by extraction with hexane and the zein is precipitated by adding the isopropyl alcohol solution to cold water. Zein, applied either in alcohol solution or aqueous suspension, is used for coating paper. Such paper is very resistant to grease and oils and is used for wrapping foods.

Zein can be used as a substitute for casein in making plastic materials. It has an advantage over casein in that it reacts so slowly with formaldehyde that the formaldehyde necessary for final hardening can be incorporated into the plastic mix along with plasticizers, pigments and extenders. After thorough mixing, the material is formed in sheets or rods and then partially cured by heating for a short time at 100° C. The material can then be punched, cut or machined and finally cured by heating at 60–100° C. (140–212° F.) for a fairly long period. Zein plastics can also be made in the same way that casein plastics are made and cured by immersing in formaldehyde solution. Hydrochloric acid is an effective catalyst for this curing process.

Zein plastics are used in the manufacture of buttons, buckles and other novelties. They show better resistance to moisture than the casein plastics.

⁵ Boyer, *Ind. Eng. Chem.* **32**, 1549 (1940).

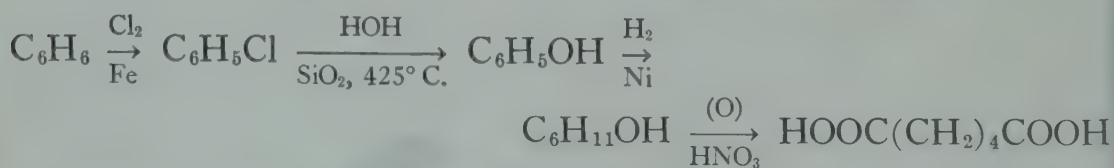
KERATIN

Keratin plastic, which may more properly be referred to as a resin extender, is being used in conjunction with urea or phenolic resins. Obtained from such miscellaneous sources as horn, hoofs, and feathers, the material is being applied in conjunction with other base resins without any decrease in the characteristics of impact strength and plastic flow.

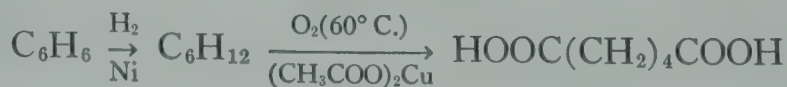
NYLON

The synthetic plastic, Nylon, is the direct result of a broad program of fundamental research, started by the DuPont Company in 1928, to learn more about the nature of polymerization and the structure of polymers. A number of high molecular weight polymers, called superpolymers (molecular weights greater than 10,000) were prepared from (a) hydroxy acids, (b) dihydroxy alcohols and dicarboxylic acids, (c) amino acids and (d) diamines and dicarboxylic acids. When one of the molten superpolyesters was being removed from a still, it was noted that the material could be drawn out as a long fiber which could be extended even further when cooled. This first fiber was not very strong, did not have much elasticity and was softened by hot water. It was a poor fiber compared with cotton, silk and wool, but it did suggest possibilities. Research showed that the superpolyamides had higher melting points than the superpolyesters and eventually an excellent fiber known as Nylon was produced. The commercial production of Nylon yarn was started early in 1940.

Manufacture.—The fundamental organic compound from which Nylon is synthesized is benzene, which in turn is obtained by the destructive distillation of soft coal. Benzene can be converted into adipic acid by first chlorinating it to make chlorobenzene, hydrolyzing the chlorobenzene to produce phenol, reducing the phenol to cyclohexanol and oxidizing this latter compound to adipic acid.

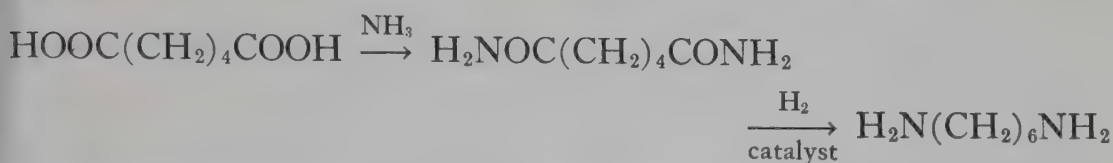


A shorter method of making adipic acid from benzene involves reduction of benzene to cyclohexane and direct oxidation of cyclohexane to adipic acid.

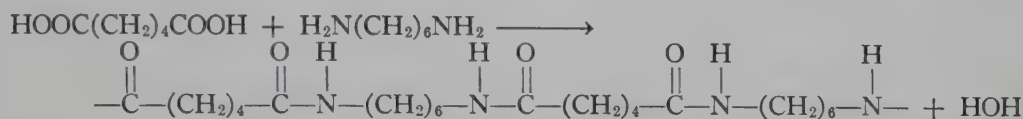


The diamine to be used for the condensation reaction with adipic

acid can be obtained from adipic acid by first making adipamide and then hydrogenating the diamide to 1,6-diaminohexane.



The polyamide is then made by heating the salt formed from the dicarboxylic acid and the diamine and vaporizing the water formed by the condensation.



In order to drive out the last traces of moisture from the viscous polymer and also to increase the length of the polymer, the reaction mixture may be heated under greatly reduced pressure (one millimeter or less). The length of the polymer can be controlled by the temperature, pressure and time allowed for the condensation reaction. It should be mentioned that Nylon is a generic term which applies to all polyamides obtained from a diamine or a mixture of diamines and a dicarboxylic acid or a mixture of dicarboxylic acids. It is thus possible to make a very large number of Nylons having substantially different properties.

An excellent illustration of the relationship between chemical structure and the properties of a polymer is found in a comparison of the polyamides formed from a dicarboxylic acid (sebacic acid) with (a) decamethylene diamine, and (b) decamethylene monomethyl diamine, $\text{H}_2\text{N}(\text{CH}_2)_{10}\text{NHCH}_3$. Although the polyamide obtained in the first case is suitable for use as a textile, the polymer obtained when decamethylene monomethyl diamine is used has definite rubber-like properties.⁶ It will be observed that all of the amide groups in

the fiber polymer are $\begin{array}{c} \text{O} \quad \text{H} \\ || \quad | \\ -\text{C}-\text{N}- \end{array}$ while in the rubber-like polymer,

some of the amide groups are $\begin{array}{c} \text{O} \quad \text{CH}_3 \\ || \quad | \\ -\text{C}-\text{N}- \end{array}$. This suggests the possibility that hydrogen bonding⁷ between the polyamide chains may

⁶ Baker and Fuller, *J. Am. Chem. Soc.*, **65**, 1120 (1943).

⁷ Chaplin and Hunter, *J. Chem. Soc.*, 1114 (1937); Copley, Zellhoefer and Marvel, *J. Am. Chem. Soc.*, **60**, 2671 (1938).

be partly responsible for the formation of a fiber, while the absence of hydrogen bonding may be desirable for the production of rubber-like properties.

Fabrication.—Nylon resins are thermoplastic polymers and the commercial modifications have melting points of about 250°C . (480°F .). They can be molded either by compression or injection molding machines, though the softening point, 235°C . (455°F .), is higher than that of other thermoplastics. It is interesting to note that some forms of Nylon have been obtained which have melting points as high as 315°C . (600°F .). Cold-rolling of molded polyamide resins increases their tensile strength. (Cf. p. 311.)

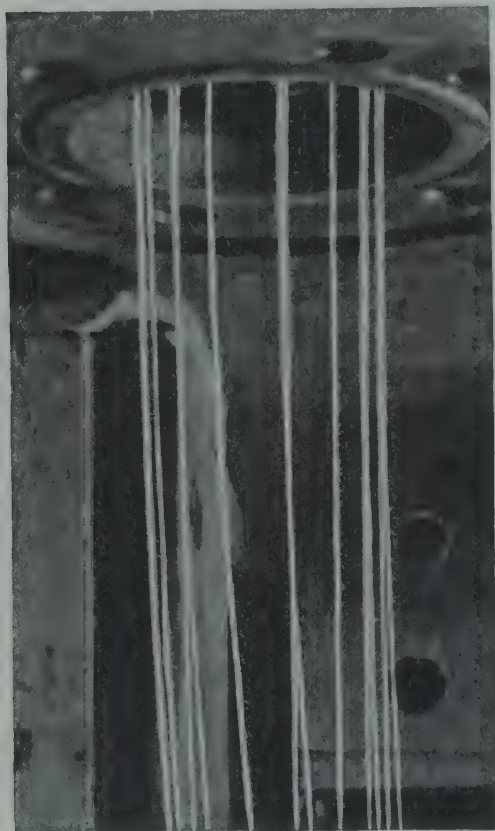


FIG. 17.1. The birth of Nylon filaments. From tiny holes in this spinneret are extruded these fine filaments of Nylon. All of the filaments shown here will be wound together to form Nylon yarn. (Courtesy Du Pont Company.)

Nylon monofilaments are made by extruding the molten polymer through orifices of any desired diameter. (See Figure 17.1.) The filament solidifies as soon as it comes in contact with cool air. These monofilaments are widely used as bristles for various types of brushes.

The most popular and most widely known form of Nylon is Nylon yarn. This yarn is composed of 30–40 or more filaments which have been obtained by forcing molten Nylon through tiny orifices in a suitable die. As the individual filaments are brought together they are twisted a few turns per inch in order to form the yarn. The properties of the yarn are greatly improved by stretching it, while cold, to four to seven times its original length. This elongation is done under low tension, by rewinding the yarn on a spool which is

revolving four to seven times as fast as the spool from which the yarn is being removed. The diameter of the yarn depends upon (1) the diameter of the openings of the spinneret, (2) the extent of cold-drawing, (3) the number of individual filaments twisted together.

The cold-drawing process appears to be a very important factor in improving the properties of Nylon. In the filaments extruded from the bath of molten Nylon, the long, polymeric molecules (10–12 millionths of an inch) are believed to be present in an unoriented, helter-skelter arrangement. The cold-drawing is believed to orient these molecules so that they all lie in the direction of the length of the fiber. This treatment causes some crystallization to occur, as illustrated in Figure 17.2B. The closeness of the molecules probably brings into play strong intermolecular forces which resist movement of the molecules past each other, thereby accounting for the high modulus of elasticity and tensile strength of the fibers. The tensile strength of the cold-drawn yarn may be 100–200% greater than that of the original yarn.



FIG. 17.2. A, X-Ray diagram of nylon fibers (type 66)—undrawn. B, X-Ray diagram of nylon fibers (type 66)—after drawing 400%. (Courtesy Du Pont Company.)

Untreated Nylon yarn possesses a high luster much greater than that of silk. The luster can be dulled by adding a finely divided white pigment, such as titanium dioxide, to the molten Nylon before spinning. Since this pigment is incorporated within the filaments, it is not removed by washing. Colored pigments can be added to the molten Nylon, but Nylon textiles are usually dyed after being formed. Many dyes which have proved satisfactory for acetate rayon have been found to be suitable for Nylon.

Properties and Applications.—One of the most outstanding properties of Nylon is its high softening point. The softening points

TABLE II-17. PROPERTIES OF TEXTILE YARNS DETERMINED AT 60% RELATIVE HUMIDITY AND 70° F.^a

	Nylon	Silk	Textile Types		High Tenacity Viscose Rayon
			Viscose Rayon	Acetate Rayon	
Dry tenacity (g/d) ^b	4.7-5.5 *	4.0-5.0	1.6-2.0	1.3-1.5	3.1-3.7
Dry elongation (%)	20-13	15-25	15-23	22-27	8-13
Wet tenacity (g/d)	4.1-4.8	3.6-4.5	0.7-1.0	0.8-1.0	1.8-2.4
Elastic recovery after 4% stretch (%)	100	50	30	50	40
Moisture absorption	3.5	11	12	6.5	12

^a Simonds and Ellis, *Handbook of Plastics*, p. 371, D. Van Nostrand Co., 1943.

^b g/d represents grams per denier.

The expression, grams per denier, is used to represent the tensile strength of a single strand of a fiber. A denier is defined as the weight, in grams, of 900,000 cm. of fiber. Since this weight will vary with the density of the fiber and its cross-sectional area, the numerical value of the denier is expressed by the equation,

$$\text{denier} = 900,000 \times D \times A$$

where D = fiber density expressed in gms. per cm.³

A = cross-sectional area expressed in cm.²

The following equations will show how it is possible to change a value expressed in gms. per denier to the corresponding value of lbs. per sq. in.†

$$(1) \frac{\text{gms.}}{\text{denier}} = \frac{\text{gms.}}{900,000 \times D \times A}$$

$$(2) \frac{1}{A} = \frac{900,000 \times D}{\text{denier}}$$

$$(3) \frac{\text{lbs.}}{\text{in.}^2} = \frac{\frac{\text{gms.}}{453.6}}{\frac{A}{2.54^2}} = \frac{\text{gms.}}{453.6} \times \frac{2.54^2}{A}$$

Substituting the value of $\frac{1}{A}$ from equation (2) in equation (3),

$$(4) \frac{\text{lbs.}}{\text{in.}^2} = \frac{\text{gms.}}{\text{denier}} \times 900,000 \times D \times \frac{2.54^2}{453.6}$$

$$(5) \frac{\text{lbs.}}{\text{in.}^2} = \frac{\text{gms.}}{\text{denier}} \times D \times 1.2791 \times 10^4$$

† Sieminski, *Rayon Textile Monthly* XXIV (11) 63(585)-65(587), (1943).

of such resins are usually between 205° C. (400° F.) and 315° C. (600° F.). The fact that Nylon yarns and monofilaments can be made which are not softened by boiling water or even by moderately superheated steam is of great value in extending its use in the manufacture of hosiery and other articles of clothing and in the fabrication of industrial brushes which may be used under hot, sterilizing conditions.

The tensile strength of Nylon resins varies from 5000 to 8500 lbs. per sq. in. This large variation depends not only on the lengths of the polymeric molecules but also on the orientation or extent of crystallization induced by cold-drawing of the fiber. The combined factors of high tensile strength and good elasticity make it a valuable textile for the manufacture of hosiery.

At ordinary temperatures, Nylon exhibits good resistance to oils, grease and organic solvents, except phenol, cresol and formic acid. It is readily disintegrated by concentrated mineral acids. Exposure of Nylon hosiery, for example, to fumes of hydrogen chloride gas, will ruin the stockings in a short time. The absorption of moisture is rather high, 7.5%, compared with other thermoplastic resins, but it is lower than that of other common textile fibers. Furthermore, Nylon can be rendered waterproof by impregnating the fabric with

stearamidomethylpyridinium chloride, $C_{17}H_{35}CONHCH_2$ .

Nylon so treated is useful for making raincoats, shower-curtains and

Similarly, the following equations illustrate the method of changing values expressed in lbs. per sq. in. to gms. per denier. From equation (3),

$$(6) \quad \frac{1}{A} = \frac{\text{lbs.}}{\text{in.}^2} \times \frac{453.6}{\text{gms.} \times 2.54^2}$$

Substituting this value of $\frac{1}{A}$ in equation (1),

$$(7) \quad \frac{\text{gms.}}{\text{denier}} = \frac{\text{lbs.}}{\text{in.}^2} \times \frac{453.6}{900,000 \times 2.54^2 \times D}$$

$$(8) \quad \frac{\text{gms.}}{\text{denier}} = \frac{\text{lbs.}}{\text{in.}^2} \times \frac{7.812 \times 10^{-5}}{D}$$

Since the value of gms. per denier is dependent upon the density of the fiber, it follows that two fibers of different densities could have the same gms. per denier values and yet have different tensile strength values, expressed in terms of lbs. per sq. in.

* Nylon yarns have been obtained with a tensile strength as high as 7 grams per denier.

TABLE III-17. PROPERTIES OF NYLON RESINS ^a

Specific gravity	1.06-1.19
Refractive index N_d	1.53
Strength, tensile, lbs./sq. in.	5,000-8,500
Modulus of elasticity, lbs./sq. in. $\times 10^5$	4.5
Strength, flexural, lbs./sq. in.	10,000-15,000
Hardness, Rockwell	L95-L100
Specific heat	.55
Softening point, ° F.	450
Volume resistivity, ohms-cm.	10^{13}
Dielectric constant, 60 cycles	3.2
Dielectric constant, 10^3 cycles	3.3
Dielectric constant, 10^6 cycles	3.6
Power factor, 60 cycles	.01
Power factor, 10^3 cycles	.015
Power factor, 10^6 cycles	.022
Water absorption, per cent in 24 hours	7.6
Elongation, per cent	30-35

^a Boonton Molding Co., *A Ready Reference for Plastics*, p. 19 (1943).

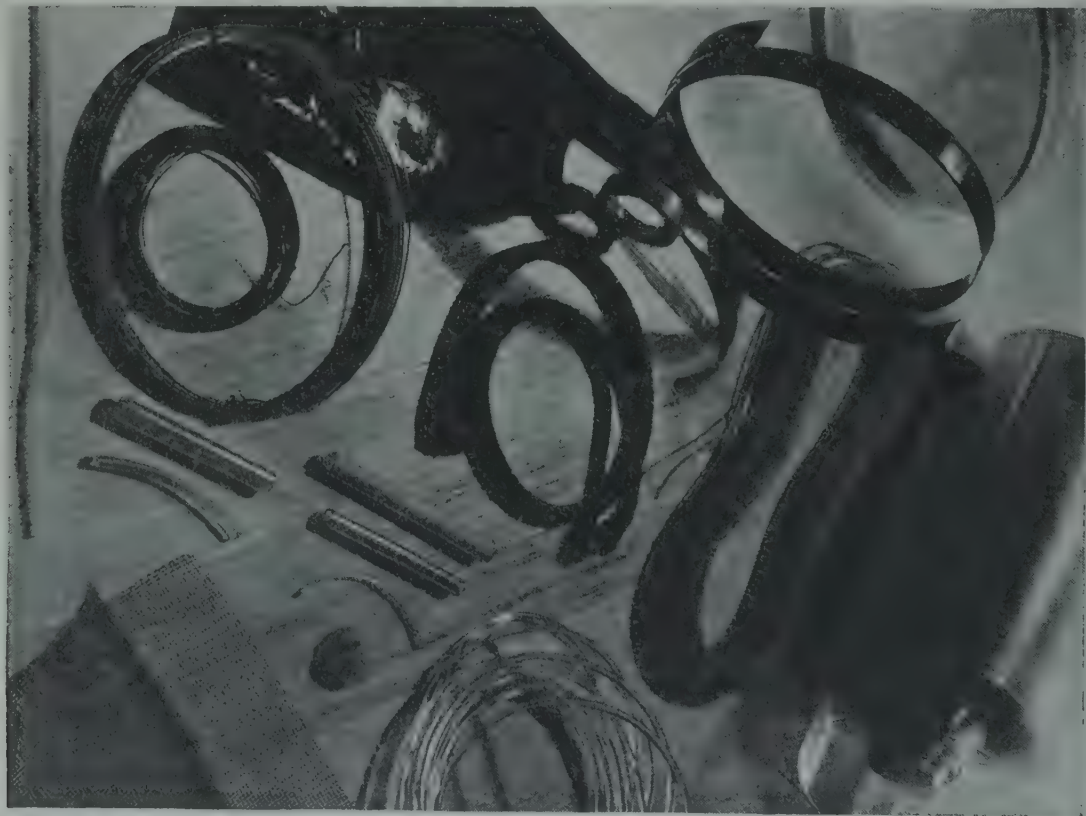


FIG. 17.3. Typical Nylon products. (Courtesy Du Pont Company.)

hospital sheeting. Nylon tends to yellow slightly when exposed to light and oxygen. Its rate of deterioration on exposure is about the same as that of other textiles. It is not attacked at all by moths and fungi. Other properties of Nylon resins are given in Table III-17.

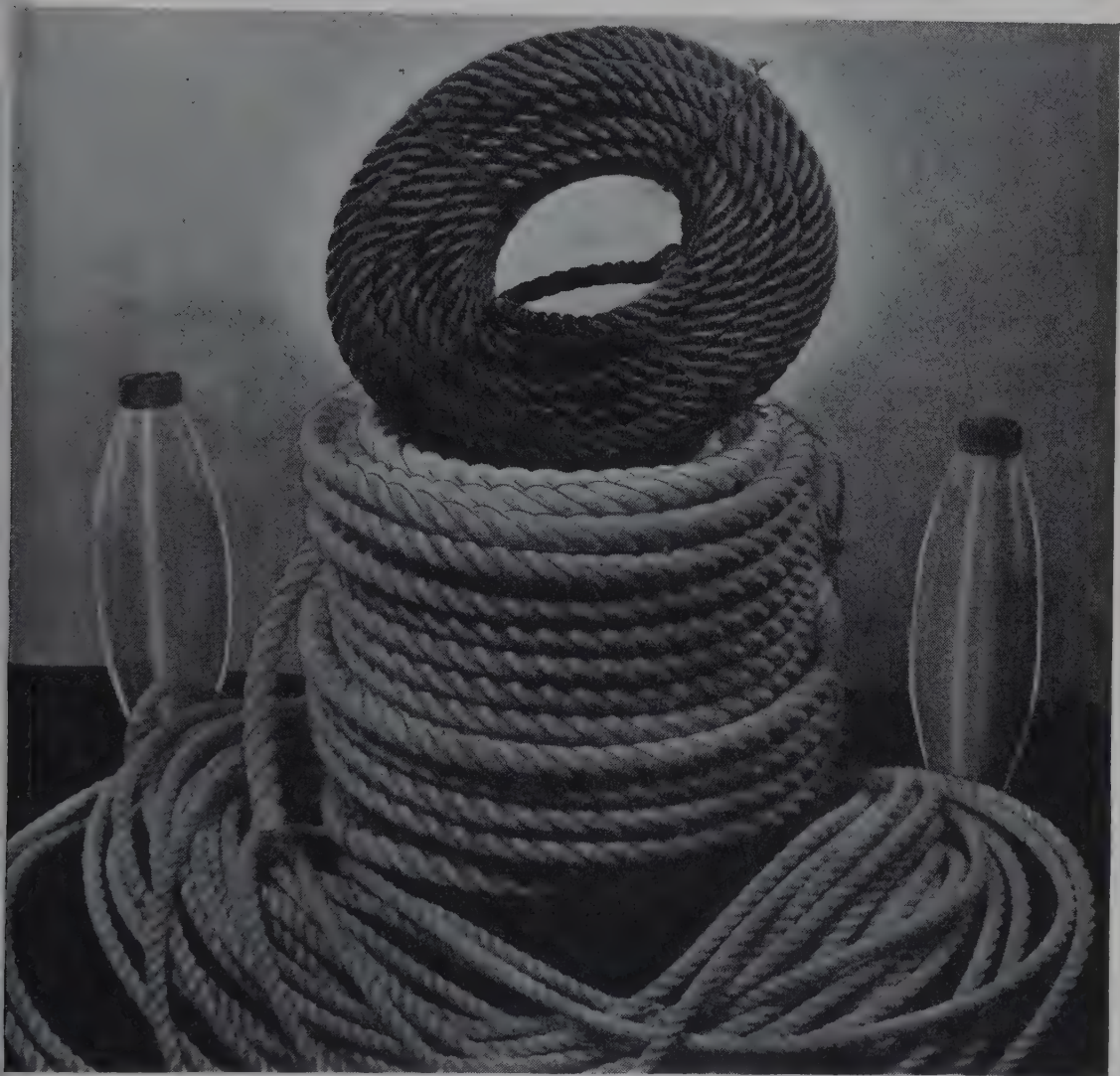


FIG. 17.4. Strong, resilient Nylon rope made from Nylon yarn, bobbins of which are shown at right and left, plays an important part in modern warfare. The olive drab dyed coil at the top is used by mountain troops as a climbing rope. The white coils are glider tow rope of two sizes. (Courtesy Du Pont Company.)

Nylon yarn has been used for the manufacture of hosiery, dress goods, lingerie, sewing thread, upholstery material, parachutes and photographic film. Nylon photographic film is cold-rolled in order to make it transparent. The thickness of this film can be half that

of the conventional films and is claimed to be much stronger than either cellulose nitrate or cellulose acetate films. It is shown in Figure 17.3 along with other products which can be made from



FIG. 17.5. In the fabrication of sweaters, short lengths of the synthetic fiber are spun into soft fuzzy threads to produce a woolly effect. (Courtesy Du Pont Company.)

Nylon plastic. One of the more recently developed uses of Nylon is in the manufacture of cord tires for use on heavy Army bombing planes. These pneumatic tires with Nylon as the cord fabric

have proven more satisfactory than any other tires for heavy duty purposes. The combined elasticity and high tensile strength have made Nylon the most suitable tow rope for use in getting gliders into the air. For this purpose, it behaves like a "giant rubber band." Nylon rope which has a diameter of one-half inch has a tensile strength of about three tons, and is exceptionally resistant to abrasion. (See Figure 17.4.) Nylon yarn is also used for wire insulation, being superior to silk with respect to abrasion resistance and high temperatures. "Nylon wool" is made by cutting filaments to the approximate length of wool staples, compressing them into bales and heating with vapors of steam or methanol. This processing sets a crimp in the staple fibers so that they possess the crimp and insulation properties similar to natural wool. (See Figure 17.5.) The crimp is claimed to be stable to dryness, moisture and heat. Such "Nylon wool" is used in making warm clothing for use in Arctic climates.

Nylon monofilaments are used extensively in making tooth-brushes, hair, nail, clothes and complexion brushes, as well as industrial brushes for many different purposes. Tennis and badminton racquet strings (Figure 17.6) are made from Nylon, and have the advantage of not being damaged by water. This material is useful for yarns, fabrics, bristles, fish lines, dental floss, surgical sutures, adhesives, electrical insulation and hose for gasoline. The surgical sutures are smoother than natural gut and consequently are less irritating, more easily removed and less likely to carry infection.

A 50-50 mixture of rubber (or synthetic rubbers such as Neoprene, Buna and Butyl) and polyamide made by dissolving rubber in the molten polymer and adding a suitable plasticizer such as *p*-toluenesulfonamide yields a film which is more resistant to moisture and oils than the unmodified polyamide.

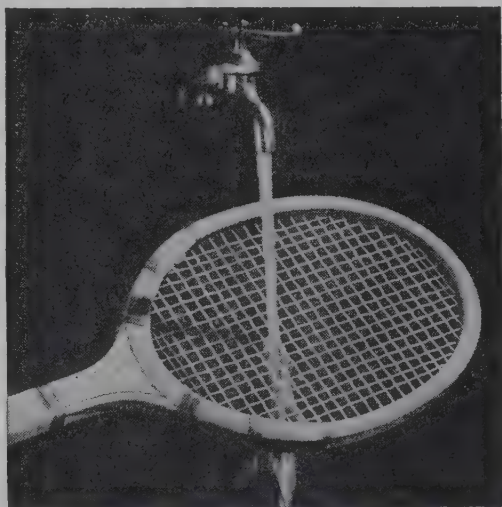


FIG. 17.6. Racket strings made of Nylon are not damaged by water. As the Nylon is a solid piece, there are no tiny strands to fray. (Courtesy Du Pont Company.)

Review Questions

1. What types of materials are included as protein plastics?
2. What theories have been advanced to explain the hardening of casein?
3. How may casein be fabricated into (a) hardened sheet, (b) fiber?
4. What are the main disadvantages of casein plastics?
5. Show by outline reactions the preparation of Nylon from benzene.
6. How is Nylon fiber produced from the polyamide?
7. What is "cold drawing" and how does it affect the properties of Nylon?

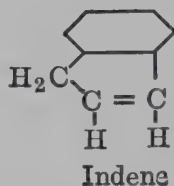
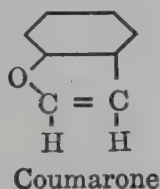
CHAPTER XVIII

SYNTHETIC PLASTICS IX: MISCELLANEOUS TYPES

In this chapter are grouped a number of synthetic plastics which should be included in a book of this type, but which hardly warrant separate chapters. Coumarone-Indene polymers, Polyterpenes, and polymeric hydrocarbons such as Naftolen and Polythene are formed as a result of addition polymerization of compounds having reactive ethylene groups, while Lignin, Chlorinated Rubber and Rubber Hydrochloride resins are products obtained by chemical modification of naturally occurring polymeric substances.*

COUMARONE-INDENE RESINS

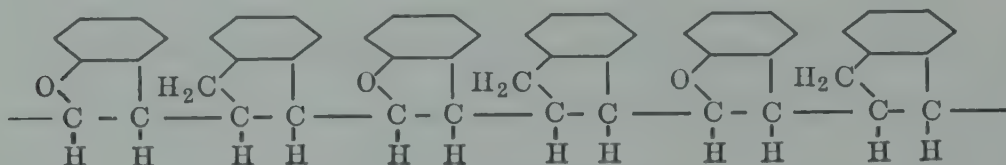
Manufacture.—These resins are produced by the polymerization of the unsaturated compounds, coumarone and indene, which are found in the light oil fraction obtained by the destructive distillation of coal. Fractional distillation of this light oil yields a coumarone fraction boiling at 168–175° C., and an indene fraction boiling at 176–182° C. Either of these fractions may be used for the polymerization, though a mixture of the two is generally used.



Since coumarone and indene both contain an ethylenic double bond, the polymerization reaction is an addition polymerization of the vinyl type. The polymerization is usually carried out in the presence of sulfuric acid as a catalyst, though aluminum chloride and other catalysts have also been used. The polymerization can be performed at temperatures ranging from -20°C . to 80°C . A resinous sludge is produced, which is allowed to settle in order to remove the acid. The resin is then washed free from acid and any unchanged light oil is removed by distillation under reduced pressure.

* A discussion of the newly-developed polymeric silicone resins will be found in Appendix I, p. 478.

Depending upon the extent of polymerization and the ratio of coumarone and indene used, the products may be hard, brittle resins or semi-fluid, viscous liquids. The formula of the co-polymer may be represented as follows:



It should not be assumed that there are alternate coumarone and indene residues in the molecule as represented by this formula. There is probably an entirely random arrangement of these units in the polymer. The hardest polymers of this class have molecular weights of approximately 1000.

Properties and Applications.—Coumarone-indene resins are not used as molding plastics themselves because of their low tensile strength and the fact that such products are too brittle for most purposes. They are used, however, as diluents and modifying agents in other plastics. For these purposes they have the advantage of being compatible with a wide variety of products such as beeswax, Halowax, candelilla and carnauba waxes, rosin, ester gum; alkyd, methacrylate, phenolic and some vinyl resins; rubber, chlorinated rubber, synthetic rubbers, asphalts and drying oils. They are soluble in aromatic and aliphatic hydrocarbon solvents, chlorinated and oxygenated organic solvents. By carrying out the polymerization in the presence of phenols, polymers having improved solubility in alcohol are obtained.

These resins exhibit poor heat resistance, low mechanical strength and they form solutions which have low viscosities. These factors are the result of the low molecular weights of the polymers. On the other hand, they have good electrical resistance and are inert toward acids, alkalies and water.

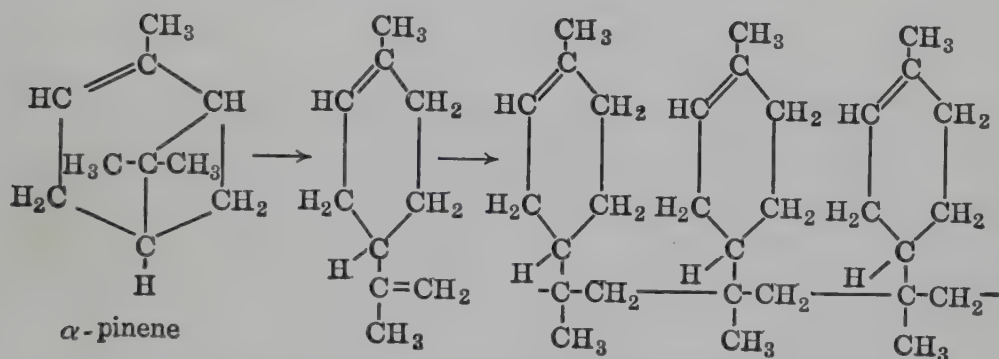
Coumarone-indene resins are used as substitutes for natural resins and ester gum in the making of varnishes. They are used in marine paint for use below the water line to prevent fouling. An interesting use is the application of a thin coating of the resin (in the form of a solution) to the surface of freshly poured concrete. This film prevents the loss of water vapor from the concrete and greatly reduces the time required for the complete hardening of the concrete. Coumarone-indene resins are also used in making printing inks, textile transfer inks, floor tiling, transcription records, artificial

leather, shoe polish; for coating high-frequency coils, impregnating paper, and as softening agents in the compounding of rubber.

The trade names of these resins are Cumar, Nevillac, Nevillite, Nevindene, Paradene and Piccoumarone. The properties of the resin are sometimes indicated by letters, as, for example, RS Cumar (rubber soft), RH Cumar (rubber hard) and VG Cumar (varnish grade).

POLYTERPENES

Polyterpenes are formed by the catalytic polymerization of α - and β -pinene which are found in turpentine. Anhydrous aluminum chloride and inorganic acids catalyze the polymerization. By proper regulation and control of this reaction, polymers can be obtained which are either friable resins or viscous liquids. The chemical changes may be represented as follows:



The molecular weights of these polymers range from 1600–2000, indicating 12–15 monomeric units. In this case, as in the case of the coumarone-indene resins, the product is heated under reduced pressure in order to distil off any unchanged monomer. This treatment raises the softening point of the resin.

Polyterpenes are relative newcomers in the field of plastics and appear to have some interesting possibilities. They are frequently used instead of coumarone-indene resins as modifying agents with other plastics. They are compatible with such resins as alkyds, polyvinyls, polystyrene, polyacrylates and phenolics. When mixed with waxes of either natural or synthetic origin, they impart both hardness and gloss. For the same reasons, they are useful in varnishes and paints. Polyterpenes are satisfactory as plasticizers and tackifying agents in the compounding of rubber and synthetic rubber for ply adhesion, coatings, and adhesives. They are soluble in aromatic and aliphatic hydrocarbons, oxygenated and chlorinated solvents. Solutions have been used satisfactorily as coatings and

these resins have replaced alkyd resins in appreciable quantities in this field. Polyterpene resins can be used in place of coumarone-indene resins to accelerate the hardening of freshly poured concrete. They are also used as paper impregnants and textile finishes. Polyterpene resins are characterized by good color and resistance to water, alkalies and acids.

The trade names used for polyterpenes are Nypene and Piccolyte.

POLYMERIZED HYDROCARBONS

Polymerized hydrocarbons are produced as a by-product of oil refining. During the refining process, unsaturated hydrocarbons are precipitated as an acid sludge by the addition of sulfuric acid. The sludge, in turn, may be freed from sulfuric acid and the unsaturated constituents separated into fractions of constant and specific properties. These hydrocarbons possess a molecular weight in the vicinity of 400 and are thus proven to be polymerization products of the original constituents of the petroleum. Depending upon the molecular weights of the polymers obtained, the products may vary from free-flowing liquids to viscous tars.

Many of the advantages of these viscous, semi-liquid resins are due to the fact that they are unsaturated hydrocarbons. Thus, when used as extenders, tackifiers, or modifiers of synthetic rubbers, these hydrocarbons may be eventually incorporated into the vulcanization procedure because of their ability to react with sulfur. The electrical characteristics and general chemical resistance are primarily a consequence of the hydrocarbon nature. Ranging in physical characteristics from materials of free-flowing liquids to tacky gums, the series is enjoying increased popularity in modifying applications. Varnishes, molding powders, adhesives, laminating mixtures, and coatings for electrical equipment may all involve the use of these hydrocarbon polymers as extenders or modifying agents. Naftolen and Duprex are commercial products of this class.

POLYETHYLENE

Polyethylene is obtained by the polymerization of ethylene at a pressure greater than 1200 atmospheres and at a temperature of 100–300° C.¹ A lower pressure (> 500 atm.) can be used if a catalyst such as oxygen (< 3%) or benzoyl peroxide is added to the ethylene.

¹ Fawcett, Gilson, Perrin, Paton and Williams, *Chem. Abs.* 32, 1362 (1938).

The commercial product is a waxy solid which melts at 110–120° C., and has a molecular weight greater than 6000. Some polymers have been made with molecular weights as high as 20,000. Polyethylene is flexible and tough over a wide range of temperatures and has a tensile strength of 1700 lbs. per sq. in. at 25° C. It possesses excellent water resistance, a 0.004 inch thick sheet transmitting only 0.4 gram of water vapor per square meter in 24 hours at 25° C.² It is not only resistant to water, but also to acids, alkalies and oxygenated organic solvents. It is soluble in aliphatic and aromatic hydrocarbons and chlorinated solvents at high temperatures. It is not greaseproof and it is usually stabilized by the incorporation of antioxidants if it is to be exposed to sunlight. Polyethylene is outstanding with respect to its electrical properties, being comparable with polystyrene as an insulating material.

Polyethylene can be fabricated by compression, injection, extrusion or calendering procedures. It can be used alone or it can be



FIG. 18.1. Made of polythene, the ice cube tray, jar top, sheeting, collapsible tube, wire insulation, tubing, bottle stopper and injection-molded grommets show some of the possible future products of this new plastic. (Courtesy Du Pont Company.)

² Shackleton, *Modern Plastics*, 21 (6), 99, 1944.

compounded with suitable resins and waxes. Increased flexibility is produced by mixing it with polyisobutylene (Vistanex) in a hot-melt. When extruded in the form of fine filaments, a thread is obtained which can be cold-drawn to form staple fibers which can be spun and woven. As in the case of nylon, the cold-drawing causes a new alignment of the molecules with an increase in the crystallinity of the product and consequent increase in tensile strength.

At present, the principal use of polyethylene is as electrical insulation. Figure 18.1 illustrates a few possible uses for polyethylene.

LIGNIN PLASTICS

Although not of synthetic origin, lignin plastics are discussed here because of their value in combination with phenol-formaldehyde resins in making molding powders, adhesives and impregnating varnishes. A powdered lignin resin can be obtained by acidifying the alkaline liquor left after the removal of lignin from wood, and washing the precipitate thoroughly with cold water. This resin can replace up to 50% of phenol-formaldehyde resin in molding powders, adhesives and impregnating varnishes. The lignin resin will react with 2–4 moles of phenol to form a black resin, which can be mixed with hexamethylenetetramine and fillers and molded in the same manner as phenol-formaldehyde resins.

A uniform mixture of lignin resin and cellulose can be used to the extent of 70–80% of a phenol-formaldehyde molding powder, producing articles which have better impact strengths than phenol-formaldehyde molding powders which contain wood-flour as the filler.

An interesting development in this field is the formation of lignin laminated products. The first step in the manufacture of these products is to heat waste wood with an alkaline lignin solution under high pressure. Acidification of this solution causes precipitation of the lignin resins intimately mixed with the cellulose fibers. The natural lignin content of the wood is increased by the lignin present in the alkaline solution used. The mixture is put through a beater such as that used in the manufacture of paper, screened, washed thoroughly with water and made into paper sheets, usually 0.015 inch thick. These sheets are cellulose containing 35–45% of lignin. Lignin resins are thermoplastic, especially so in the presence of moisture which acts as a plasticizer. These sheets may be laminated without the addition of any other resin by applying the full hydraulic pressure first (1500–2000 lbs. per sq. in.), to avoid driving out the water until the desired shape is obtained, and then heating to 135–

182° C. (275–360° F.). These laminated sheets are available in thicknesses from 1/64"–2" and they can be machined by the usual methods. They have good mechanical strength, excellent electrical properties and low moisture absorption. They are used for switchboards, switch bases, connection blocks, insulating spaces, insulating washers, insulating supports, ice-cube trays, ice boxes, filing cabinet rollers, desk drawer runners, work table tops and foundry patterns. Figure 18.2 illustrates some electrical insulation parts made from laminated lignin sheets.

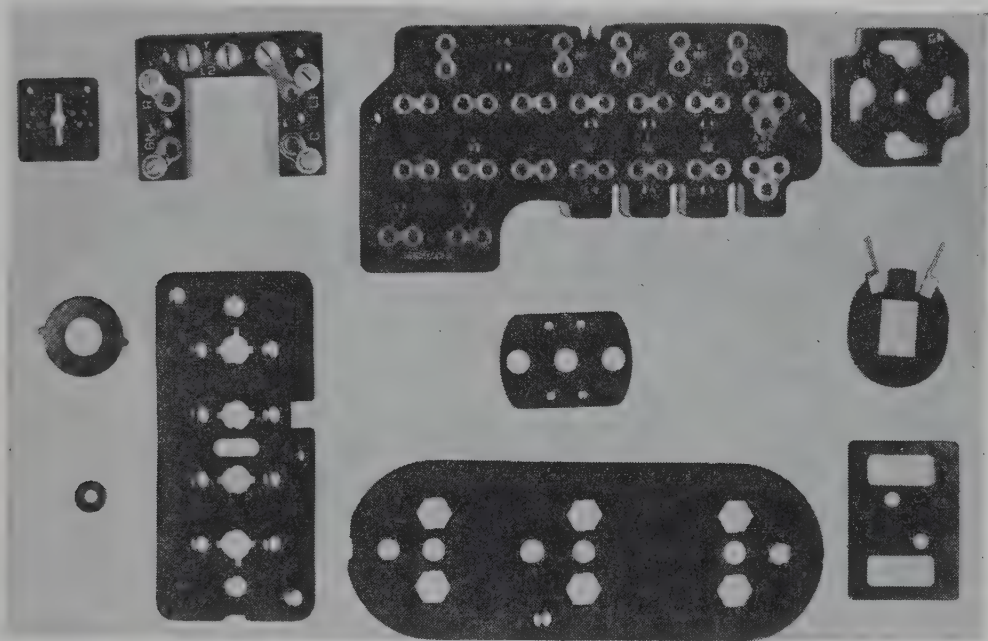


FIG. 18.2. Electrical insulation parts fabricated from laminated lignin sheets (Lignolite). (Courtesy of Marathon Corporation, Chemical Division.)

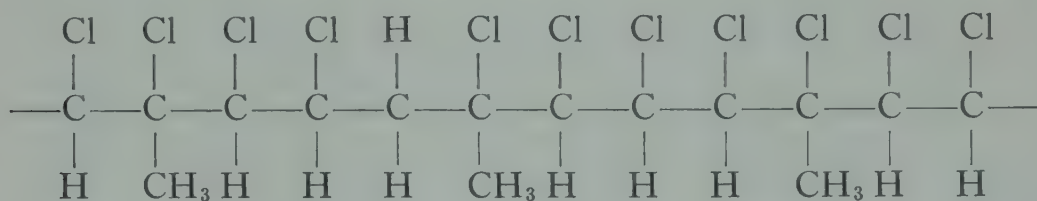
If desired, the lignin-cellulose sheets can be coated with 8–15% of phenol-formaldehyde resin and then laminated by the usual procedure. This type of laminated product is more resistant to water than the lignin laminated material. It is used for table tops, wall panels and decorative purposes.

CHLORINATED RUBBER

Manufacture.—Although chlorinated rubber can be obtained by exposing thin sheets of rubber to either liquid or gaseous chlorine, it is usually made by passing chlorine gas into a colloidal solution of rubber in a suitable solvent such as carbon tetrachloride, chloroform, acetylene tetrachloride, carbon disulfide or benzene. In order to

decrease the viscosity of the chlorinated rubber solution, the rubber may be milled at 80° C. or higher, prior to chlorination.³ A further improvement which decreases the viscosity of the final solution and also leads to the formation of a purer product is the removal of water. This is done by refluxing the rubber solution, before chlorination, for 8–48 hours. This treatment decreases the size of the particles and the water is removed by allowing some of the vapors to escape. If desired, non-rubber, haze-forming impurities may be removed by the addition of 1% of adsorbent carbon and filtering.⁴

The reaction between rubber and chlorine is exothermic. The reaction kettle can be cooled with water or the rate of addition of chlorine can be controlled so that the heat of reaction is absorbed in refluxing the solvent. The chlorination is continued until the desired amount of chlorine has been introduced. Commercial products usually contain approximately 66% of chlorine. This high percentage of chlorine indicates that substitution as well as addition has occurred. A compound having the empirical formula $C_5H_7Cl_3$ contains 61.4% Cl while $C_5H_6Cl_4$ contains 68.2% Cl. From these data, it appears that the formula for chlorinated rubber may be represented as follows:



After the chlorination is complete, the hydrogen chloride and any unreacted chlorine can be removed by boiling or by blowing air through the solution. The last portions of hydrogen chloride are neutralized by the addition of a slight excess of calcium oxide, followed by filtration or decantation. The chlorinated rubber can be precipitated by adding the solution to petroleum hydrocarbons in which the chlorinated rubber is insoluble. It can also be precipitated by adding the solution to boiling water, preferably containing some ethyl alcohol or methanol. In this procedure, the organic solvent is vaporized by the boiling water and the chlorinated rubber separates in the aqueous solution. The product is then dried before use.

Properties and Applications.—Chlorinated rubber is a tasteless, odorless, incombustible white solid which is non-toxic, infusible and

³ North, U. S. Patent 2,148,830 (1939).

⁴ Raynolds, U. S. Patent 2,247,407 (1941).

chars at about 150° C. It is soluble in a variety of solvents, such as aromatic hydrocarbons, certain hydrogenated naphthas, chlorinated hydrocarbons, esters and ketones, except acetone. It is insoluble in water, alcohols, turpentine and some aliphatic hydrocarbons.

Films made from unplasticized chlorinated rubber have excellent resistance to acids, alkalies, water, salt solutions, alcohols and aliphatic hydrocarbons, but suffer from the disadvantage of being brittle. The incorporation of various plasticizers in the resin decreases the brittleness, but also decreases the resistance of the film or coating to the chemicals listed above. Plasticizers which have been used successfully are chlorinated biphenyl, hydrogenated methyl abietate, chlorinated paraffin, methyl phthalyl ethyl glycolate, glycol stearates such as butyl cellosolve stearate and butyl carbitol stearate, ester gum and dammar.

Because of its non-flammability and high resistance to moisture and chemicals, chlorinated rubber is used in fire-resistant coatings, chemical-resistant paints and finishes, concrete coatings and traffic-marking paints. It is also used in making moisture-proof paper and cloth coatings, wood finishes, heat-sealing paper coatings, artificial leather dopes and printing inks.⁵ Chlorinated rubber is widely used for improving the adhesion and impermeability of alkyd resins which are either air-dried or baked at low temperatures. It has been found that alkyd resins made from dialcohols and diacids having long chains are more compatible with chlorinated rubber than alkyd resins having a comparable degree of esterification and made from lower molecular weight dialcohols and diacids.

Although pure chlorinated rubber is not thermoplastic, a properly plasticized product can be obtained which is a powder at room temperature and which can be molded at elevated temperatures and pressures.

Trade names for chlorinated rubber are Parlon and Raolin.

RUBBER HYDROCHLORIDE

Manufacture.—Rubber hydrochloride is made by the addition of hydrogen chloride to a solution of rubber in a suitable solvent such as toluene, benzene, chloroform or other chlorinated hydrocarbon. In an earlier process⁶ the reaction was carried out at room temperature or at slightly elevated temperatures and pressures. A more recent development⁷ involves the addition of hydrogen chloride at

⁵ Reynolds, Radcliffe and Vogel, *Ind. Eng. Chem.* **34**, 466 (1942).

⁶ Bradley and McGavack, U. S. Patent 1,519,659 (1929).

⁷ Winkelmann, U. S. Patent 2,047,987 (1936).

low temperatures, -10°C. to -78°C. , and under a pressure of about 70 lbs. per sq. in. It was found that the lower the temperature employed the better the clarity of the film produced. Practical commercial temperatures are from -10°C. to -35°C. The addition of hydrogen chloride is continued until the chlorine content is 29–30.5%. The solution is then allowed to warm up to room temperature and is neutralized immediately with sodium carbonate, ammonia or some other alkali. Rapid removal of the excess acid also improves the clarity of the film eventually produced. The rubber hydrochloride is then precipitated as a white, amorphous powder by adding the solution to ethyl alcohol. After washing and drying, it is dissolved in a suitable solvent or mixture of solvents, the solution filtered, and then deposited on a band-type machine in order to form a thin film.

It should be mentioned that the nature of the rubber used for hydrochlorination and the milling to which it is subjected have an effect on the color and strength of the film.

Properties and Applications.—Films of rubber hydrochloride containing more than 30.5% of chlorine are brittle and stiff and tend to crack when flexed, while those containing less than 28–29% of chlorine are apt to be soft and sticky at room temperature. Even films containing 29–30.5% of chlorine will become brittle when exposed to sunlight, and consequently are not very satisfactory for wrapping purposes. However, the useful life of rubber hydrochloride films can be increased 10–15 times by the addition of suitable stabilizing agents. For this purpose a mixture of 1.5% hexamethylenetetramine and 3% dicyclohexylamine has proved quite satisfactory. Ditetrahydrofurfurylamine can be used in place of dicyclohexylamine. From 2–20% of oxides and carbonates of metals such as magnesium, calcium, aluminum, sodium and barium act as stabilizers. The alkaline stabilizing agents are believed to act by neutralizing the small amounts of hydrogen chloride that are produced by the photochemical decomposition of rubber hydrochloride and thus prevent the deleterious effects produced by the free hydrogen chloride in the film. Other stabilizing agents which have been used are pine oil, which contains compounds having unsaturated linkages to which hydrogen chloride can add; ferric oxide, carbon black and aluminum powder. A possible explanation of the value of aluminum in preventing decomposition and consequent brittleness is that aluminum may reflect ultraviolet light to such an extent that photochemical decomposition occurs only slowly. In the case of carbon black, the particles of carbon may absorb the

short wave lengths of light and convert them to longer, less harmful wave lengths.⁸

Plasticizers are also valuable in improving the tear resistance and durability of rubber hydrochloride films. Butyl stearate, dibutyl phthalate, triphenyl thiophosphate and chlorinated paraffin are typical plasticizers for these films. Most plasticizers also cause a decrease in moisture resistance. However, a rubber hydrochloride film containing 8% butyl stearate and 2% paraffin showed improved moisture resistance, as well as improved tear resistance and increased durability when compared with an un-plasticized film.

Rubber hydrochloride films are characterized by good elongation, tear-resistance and resistance to moisture. Because of its good moisture resistance, it is used for enclosing a complex machine such as an airplane engine to protect it from rusting during shipment. As additional protection, a silica gel adsorbent is placed inside the package. The material can be sewed like cloth and hence is used in making garment bags (Figure 18.3), raincoats, shower curtains and umbrellas. It is also used for lining bottle caps and packaging both dry and wet foods. Rubber hydrochloride softens at 110–120° C., and when heated under pressure, two pieces can be sealed firmly together. Rubber hydrochloride products are sold under the trade name Pliofilm.

Chlorinated Rubber Hydrochloride.—A chlorinated rubber hydrochloride is made by dipping sheets of pale crepe paper of approximately 0.02" thickness first into liquid hydrogen chloride at - 85° C. for 3–4 minutes and then into liquid chlorine at - 40° C. for 2–4 minutes. The product dissolves readily in

⁸ Holden, U. S. Patent 2,136,342 (1938).

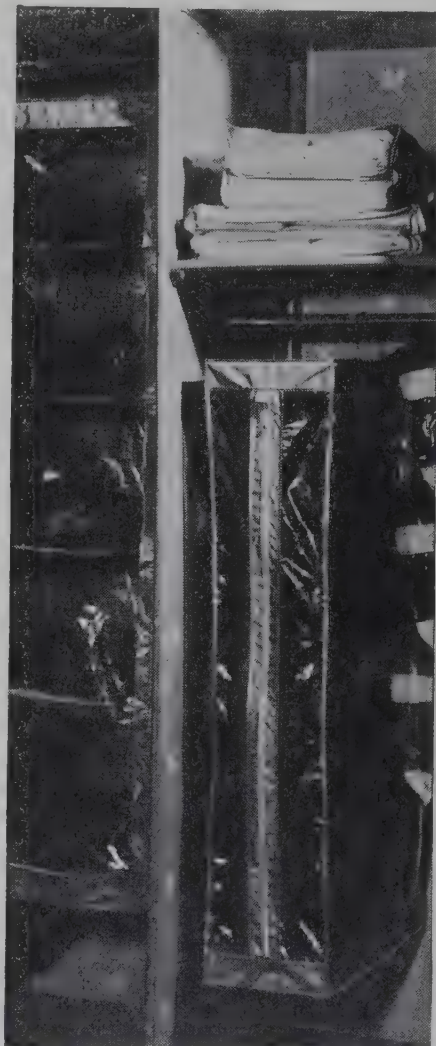


FIG. 18.3. Pliofilm^a garment bags. (Courtesy of Goodyear Tire and Rubber Company.)

^a Registered trade mark of Goodyear Tire and Rubber Company.

benzene and chlorinated hydrocarbon solvents. These solutions are suitable for making transparent sheets and films of 0.001" thickness which are useful for wrapping purposes.

Review Questions

1. Show by a structural formula the composition of:
 - (a) Coumarone-Indene resins
 - (b) Polyterpenes
 - (c) Polyethylene
 - (d) Chlorinated rubber.
2. List two outstanding properties and one commercial application of each resin included in the miscellaneous classification.
3. Describe the preparation of chlorinated rubber.
4. Why is polyethylene important in the electrical field? What comparisons may be drawn between the structure, moisture resistance and electrical properties of both polystyrene and polyethylene?

CHAPTER XIX

SYNTHETIC PLASTICS X: SYNTHETIC RUBBERS

A brilliant chapter is being written into the annals of organic research by the successful endeavors to produce materials which duplicate natural rubber in performance. Stimulated by an effort to attain economic and national independence of the natural supply of rubber, the scientists of many countries have jointly built up an amazing storehouse of data on the structure and behavior of both natural and synthetic rubbers.

The classical attempts to produce a synthetic rubber were based upon the knowledge that rubber is composed of repeated isoprene units. Faraday, in 1826, showed that rubber is composed of carbon and hydrogen only, and in 1860 Grenville Williams identified the hydrocarbon unit in rubber as isoprene, C_5H_8 . This material was produced as a result of the thermal decomposition of rubber. The polymeric structure of the macromolecule was suggested by Bouchardat (1879) after he had obtained a product which resembled rubber in elasticity and rebound while working with isoprene. The first intentional synthesis of rubber, however, is credited to Tilden who, in 1892, produced isoprene from turpentine and then formed a rubbery product which was similar to rubber in many respects but lacking in sufficient strength to be of any value. Accelerated methods for converting isoprene to rubber were used by Hofmann and Coutelle and independently by Harries. One of the best methods of accelerating the conversion of the simple hydrocarbon molecule to the giant molecule—that of catalysis by sodium—was announced soon after by Matthews and Strange.

Interest, to this time, had been centered chiefly upon the polymerization of isoprene. Clear evidence that the isoprene molecule is not necessary was provided, however, when "methyl rubber," produced from 2,3-dimethylbutadiene ($CH_2=C-C=CH_2$), first



appeared. Preconceived ideas of raw materials necessary were rapidly modified as production of a synthetic rubber by the use of this hydrocarbon advanced. During World War I, approximately 2350 tons of this product were formed in a German-operated plant.

Difficulties of preparing the raw materials and adapting the inferior rubber to the usual processing methods caused abandonment of this project, but evidence that isoprene is not unique in its ability to form rubber-like products was well illustrated.

Developments, after the war, followed one another in rapid succession. Advances in knowledge of the structure, physical behavior and theories of internal arrangements changed the problem from that of producing a material which would duplicate natural rubber to that of synthesizing a product which would resemble rubber in its performance. The same characteristics of elasticity and retroactivity were sought. Greater variation in choice of raw materials was permitted and the only requisites were those concerned with final properties. Thus, actually, the problem changed from synthesizing rubber to replacing rubber. Investigation continued to be centered about the application of dienes, however, and, because of its newly-developed sources of availability, butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) became the subject of intensive research. About 1910, Lebedev obtained a rubber-like product from the polymerization of butadiene by heating at 150°C . in a bomb. Further investigation of the polymerization of butadiene was carried on by Russian chemists, particularly by Ostromysslensky and Lebedev. During the same period, German scientists were experimenting with "Buna" rubbers, i.e., rubbers obtained by the polymerization of butadiene using metallic sodium as the catalyst. In fact, the word "Buna" is composed of the first two letters of butadiene and the first two letters of the Latin word for sodium which is natrium. Butadiene was used in the formation of Buna 85 and 115.

Still broader fields were developed when 2-chlorobutadiene ($\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$) or chloroprene was utilized in the formation



of Du Pont's Neoprene and when Patrick demonstrated that rubber-like products may be formed by a condensation reaction between dihalides, the simplest being ethylene dichloride ($\text{C}_2\text{H}_4\text{Cl}_2$), and sodium tetrasulfide. The latter reaction is of particular interest in the history of synthetic rubber manufacture for it illustrates the use of a condensation reaction in a field which is otherwise devoted to addition polymerizations. Work on these three basic types, Buna, Neoprene and Thiokol, gradually resulted in improvements in preparative methods and sources of raw materials. In view of the fact that these products have compositions which are very different from the composition of natural rubber, it has been proposed that they b

called elastomers. The rubber-like products were adaptable because of their physical characteristics and improvements were made as shortcomings were detected. Evidence of the scope of development in the polymerization of butadiene derivatives is provided by the data in Table I-19, which show the effect of substitution in the basic system, $C=C-C=C$, and the fundamental importance of the structure of the monomer in determining the characteristics of the polymer produced.

TABLE I-19. ESTIMATED RELATIVE SPEEDS OF POLYMERIZATION OF VARIOUS DIENES AT 25° C., COMPARED WITH ISOPRENE ^a

Position and Nature of Substituent	Estimated Speed	Character of Polymer
$C_1=C_2-C_3=C_4$		
..... Cl Cl 	2000	Hard, not extensible
..... I 	1500	Rubber-like under certain conditions
..... Br 	1000	Good rubber
..... Cl 	700	Excellent rubber
..... Cl CH ₃	500	Fair rubber, but low extensibility
Cl Cl Cl 	120	Soft, elastic
..... C ₆ H ₅	90	Soft
CH ₃ Cl 	30	Soft
C ₂ H ₅ Cl 	30	Soft
C ₄ H ₉ Cl 	10	Soft
C ₇ H ₁₅ Cl 	10	Soft
..... C ₇ H ₁₅	9	Soft
Cl 	7	Soft, sticky
..... CH ₃ CH ₃	3	Fair rubber, but low extensibility
CH ₃ CH ₃ Cl 	1.5	Soft
..... CH ₃	1.0	Fair rubber
.....	0.8	Fair rubber
CH ₃	0.3
CH ₃ CH ₃	Probably < 1
CH ₃) ₂	↓
CH ₃
CH ₃
CH ₃) ₂
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CH ₃ CH ₃ CH ₃ CH ₃	
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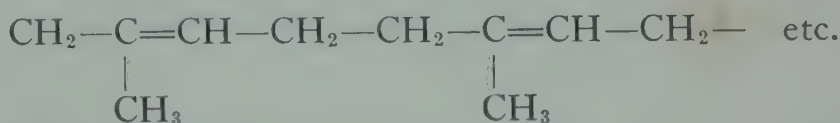
^a Carothers, *Ind. Eng. Chem.* 26, 32 (1934).

Continued work also proved that copolymerization of the diene molecules with other materials often resulted in improved rubber-like characteristics. Investigation showed that styrene and acrylonitrile were especially valuable for copolymerization with butadiene, and the production of Buna S and Buna N synthetic rubbers resulted. Also, the discovery of the occurrence of rubber-like properties in high molecular weight saturated hydrocarbons and the availability of isobutylene, $\text{CH}_2=\text{C}-\text{CH}_3$, led to the development of non-vulcanizable



products known as Oppanol or Vistanex. Later, some unsaturation was introduced into the polyisobutylene molecules by the use of a diene, butadiene or isoprene, in the polymerization to produce Butyl rubber. Isobutylene, therefore, is a raw material applied at present to synthetic rubbers of both the vulcanizable and non-curing types.

Even greater divergence from the fundamental, unsaturated, vulcanizable structure of rubber:



is introduced by the classification of such plastic masses as Geon and Resistoflex as synthetic rubbers. Again, the only basis upon which such materials may be judged "synthetic rubbers" is the fact that under certain conditions some of their properties have some resemblance to the corresponding properties of rubber.

A summary of the industrial synthetic rubbers is contained in Table II-19.

This variety of synthetic rubbers makes practically any choice of properties combinations possible. In certain respects the synthetic rubbers produced are superior to natural rubber; in others, natural rubber excels. As an example of the former, oil resistance and aging characteristics of synthetic rubbers are generally much better than those of natural rubber. In the latter category, the strength and adaptability to a broad range of temperatures of natural rubber are superior to those of any synthetic rubbers yet developed. In this connection, however, it should be emphasized that the technology of synthetic rubbers is in its infancy compared with the technology of natural rubber. Structurally, no synthetic rubber approaches natural rubber. Although some exhibit crystallinity when stretched, as in the case of rubber, study of the internal structure has shown that synthetic rubbers of the butadiene type characteristically have a

TABLE II-19. INDUSTRIAL SYNTHETIC RUBBERS






Monomer		Structure of Polymer	Trade Names	Vulcanization Agents
Formula	Name			
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	1,3-Butadiene	$(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_n$	Buna 85 Buna 115 Russian types SKA, SKB	Sulfur + accelerators
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ + 	1,3-Butadiene + Styrene	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-$ 	Buna S Hycar OS GR-S	Sulfur + accelerators
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ + $\text{CH}_2=\text{CHCN}$	1,3-Butadiene + Acrylonitrile	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-$ 	Buna N Perbunan Perbunan Extra Hycar OR Chemigum GR-N	Sulfur + accelerators
$\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$ 	2-Chloro-1,3-butadiene (Chloroprene)	$-(\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2)_n-$ 	Neoprene (GR-M) (Type designated by letters: CG, GN, FR, KN, E, etc.) Souprene, Mustone	ZnO MgO (Sulfur in special cases)

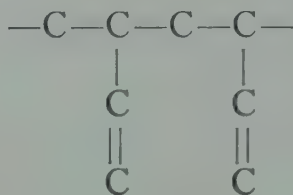
TABLE II-19 (continued)

Monomer		Structure of Polymer	Trade Names	Vulcanization Agents
Formula	Name			
$\text{ClCH}_2\text{CH}_2\text{Cl}$ $+$ Na_2S_4	Ethylene dichloride $+$ Sodium polysulfide	$\begin{array}{c} \text{S} \\ \\ -\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}_2- \\ \\ \text{S} \end{array}$	Thiokol A	ZnO $+$ Sulfur as accelerator
$\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ $+$ Na_2S_4	2,2'-Dichlorodiethyl ether (Chlorex) $+$ Sodium polysulfide	$\begin{array}{c} \text{S} \\ \\ -\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{S}-\text{S}- \\ \\ \text{S} \end{array}$	Thiokol B GR-P	ZnO $+$ Sulfur as accelerator
$\text{CH}_2=\text{C}-\text{CH}_3$ $ $ CH_3	Isobutylene	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{C}- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Vistanex Oppanol	Not vulcanizable
CH_3 $ $ $\text{CH}_2=\text{C} + \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$ $ \quad $ $\text{CH}_3 \quad \text{CH}_3$ 98% 2%	Isobutylene $+$ 2-Methyl-1,3-butadiene (Isoprene)	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Butyl (GR-I)	Sulfur $+$ special accelerators

TABLE II-19 (continued)

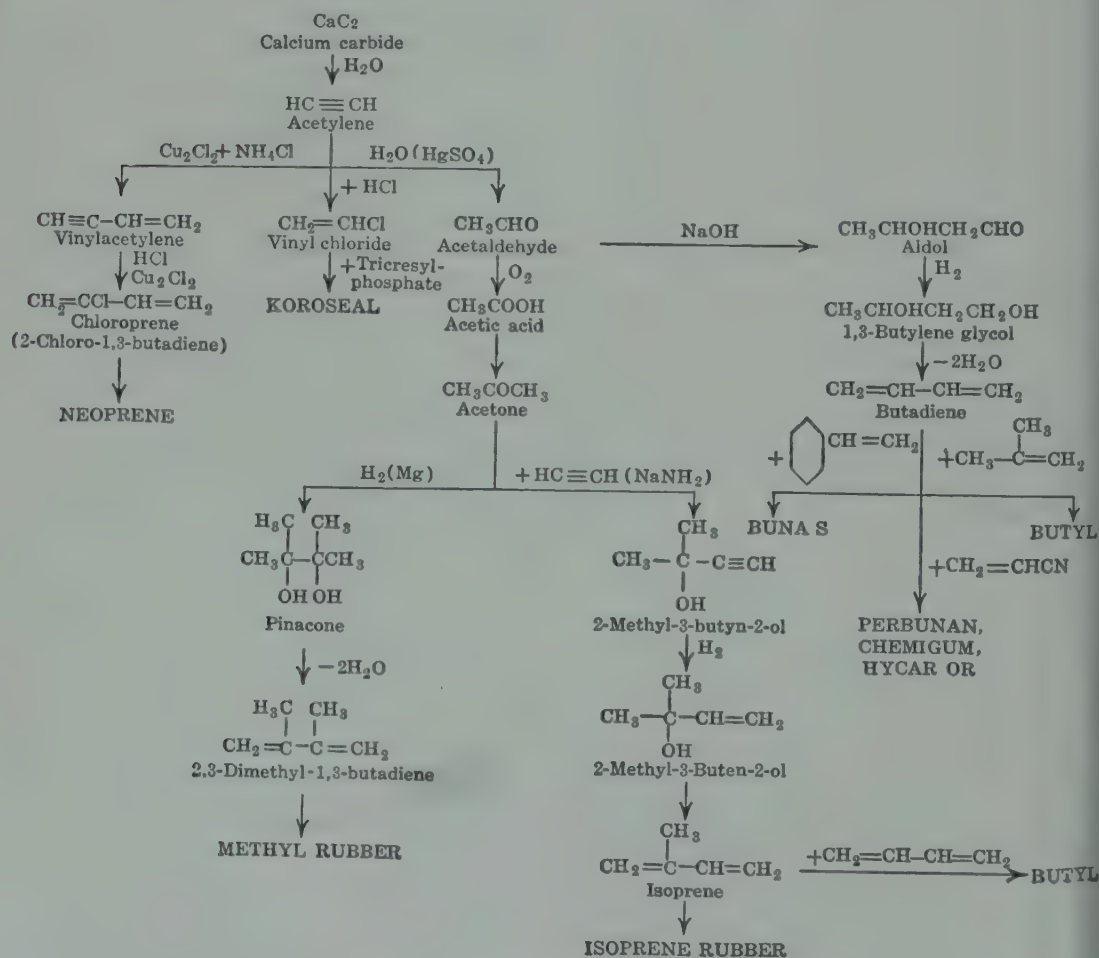
Monomer		Structure of Polymer	Trade Names	Vulcanization Agents
Formula	Name			
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{Cl} \end{array}$	Vinyl chloride	$\begin{array}{c} -\text{CH}_2\text{CHCH}_2\text{CH}- \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	Koroseal Flamenol	Not vulcanizable
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{C}=\text{O} + \text{RCHO} \\ \\ \text{CH}_3 \end{array}$	Vinyl acetate polymerized, hydrolyzed and then treated with an aldehyde	$\begin{array}{c} -\text{CH}_2\text{CHCH}_2\text{CH}- \\ \quad \\ \text{O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{R} \quad \text{H} \end{array}$	Polyvinyl acetals	Not vulcanizable, but heat-set with phenolic or urea resins
$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} + \text{H}_2\text{O}$	Vinyl acetate polymerized and then hydrolyzed	$\begin{array}{c} -\text{CH}_2\text{CHCH}_2\text{CH}- \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Polyvinyl alcohol Resistoflex	Not vulcanizable, but partially heat-set by cyclization with special agents

shorter identity period along the fiber axis than natural rubber, lack the typical *cis* arrangement of double bonds (see p. 38), but probably have a mixture of *cis* and *trans* arrangements, and are composed of a yet-undetermined proportion of 1,2 linkages which produce chain structures such as

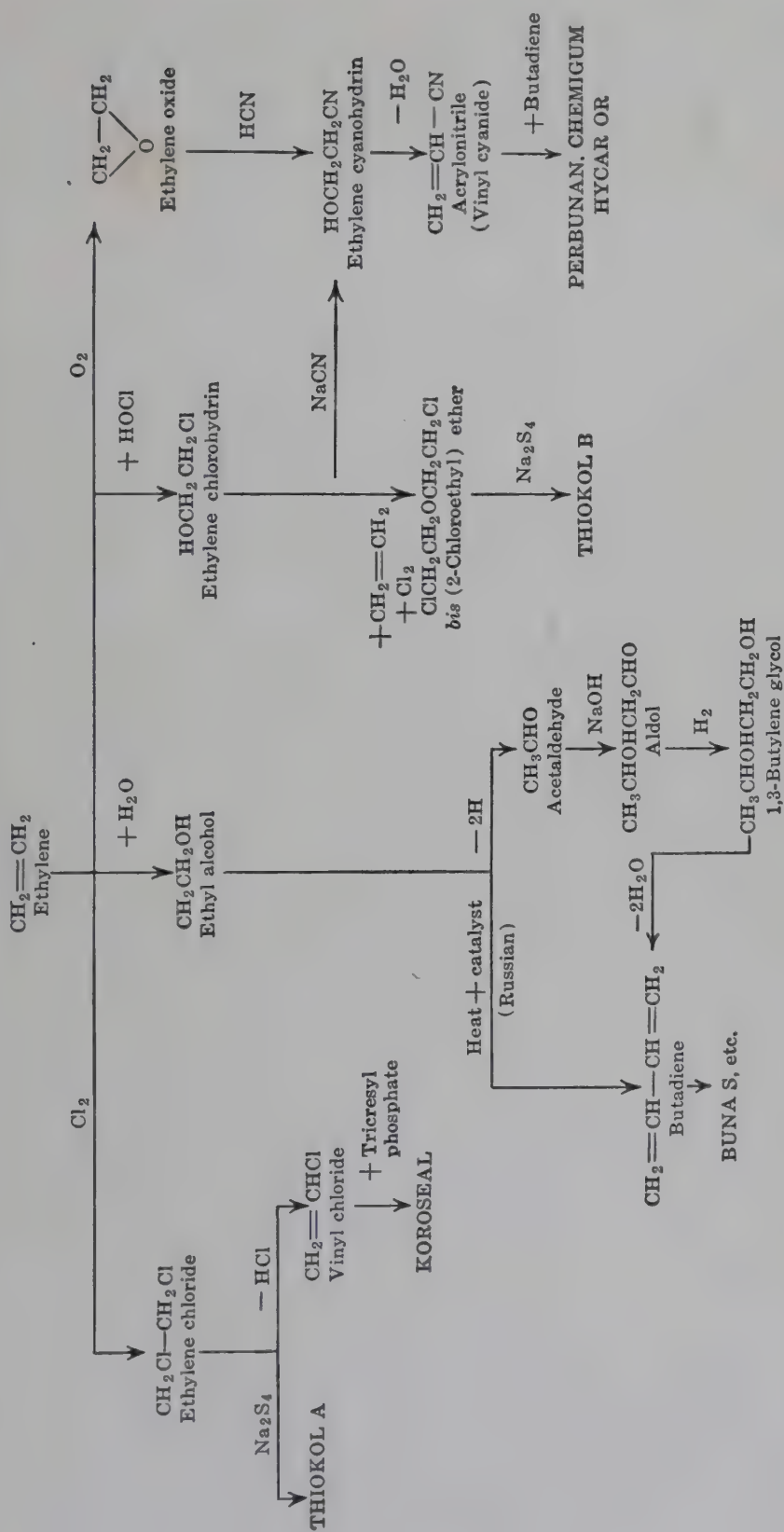


Manufacture.—The importance of synthetic rubbers to any country lies in their availability and, in turn, this factor becomes dependent upon the raw materials used in their manufacture. It is

TABLE III-19. FLOW SHEET OF SYNTHETIC RUBBERS PREPARED WITH CALCIUM CARBIDE AS THE STARTING MATERIAL.^a



^a H. L. Fisher, *Ind. Eng. Chem.* 34, 1384, 1942.

TABLE IV-19. FLOW SHEET OF SYNTHETIC RUBBERS PREPARED WITH ETHYLENE AS THE STARTING MATERIAL.^a^a H. L. Fisher, *Ind. Eng. Chem.* **34**, 1386, 1942.

not surprising, therefore, to find such abundant materials as coal, petroleum, limestone, grain, air, and water as the starting ingredients. Butadiene, for example, may be produced in this country directly from petroleum during the cracking process or from alcohol obtained by fermentation of grains. Shortages of both these materials in Germany, on the other hand, have caused recourse to the method of making butadiene from acetylene. The preparation of various synthetic rubbers from calcium carbide or ethylene (obtained by the cracking of petroleum) is shown in Tables III-19 and IV-19.

After the manufacture of the monomeric ingredients, the second step in the process, namely polymerization, may be conducted by a variety of means. The three general methods of solution, mass, and emulsion polymerization are available. The first is rarely used; the second is applied to some extent in the polymerization of butadiene types under the influence of sodium and, more generally, in the low-temperature polymerization of isobutylene. Emulsion polymerization is by far the most popular method used because of the ease with which the temperature is controlled and because of the fact that a latex or dispersion of the final product in water is thus produced. Butadiene, alone or with co-monomers; chloroprene; or the ingredients necessary for the manufacture of Thiokol may, therefore, be allowed to react after emulsification with such common emulsifying agents as oleates and sulfonates. When solid rubber is desired, it may be obtained by coagulation of the synthetic latex and purification of the coagulated material. The usual factors which cause modification of the fundamental characteristics of a polymer apply to these polymerizations.

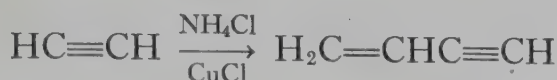
Each basic type of synthetic rubber which is of major importance in industry today will be discussed individually. It must be remembered that changes in the chemical structures of these synthetics as compared to rubber involves modification of the processing and compounding methods. Special notes on compounding may be included in each case but, for the sake of comparison, compounding of natural rubber should be reviewed at this time. (See Chapter VIII.)

NEOPRENE

This product was first introduced by the Du Pont Company in 1932 under the name, Duprene. The investigation which led to the development of this polymer was based upon the researches of Dr. Nieuwland on the reactions of acetylene. Dr. Nieuwland's pioneer

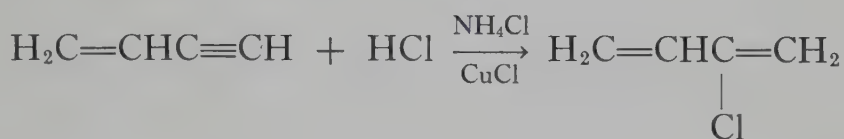
work in this field led to his association with Dr. Carothers of the Du Pont Company in developing the synthesis of polychloroprene.

It was found that acetylene could be polymerized to vinylacetylene by passing it into a solution containing ammonium chloride and cuprous chloride.



Some divinylacetylene, $\text{H}_2\text{C}=\text{CHC}\equiv\text{CCH}=\text{CH}_2$, is formed along with the vinylacetylene. The amount of divinylacetylene formed can be decreased by passing the acetylene through the catalyst solution rapidly. Unchanged acetylene (b.p. -88°C .) is separated from vinylacetylene (b.p. 5°C .) by condensing the latter.

Hydrogen chloride adds to vinylacetylene in the presence of cuprous chloride and ammonium chloride to form 2-chloro-1,3-butadiene (chloroprene). This addition must be controlled carefully in order to prevent, as far as possible, the addition of a second molecule of hydrogen chloride to form 1,3-dichloro-2-butene.



The addition of hydrogen chloride to butadiene appears from the equation to be a 1,2 addition to the triple bond. However, when concentrated hydrochloric acid is shaken with vinylacetylene, the product is 4-chloro-1,2-butadiene, $\text{ClCH}_2\text{CH}=\text{C}=\text{CH}_2$ indicating that 1,4 addition has occurred. This product rearranges to form the 2-chloro-1,3-butadiene isomer fairly rapidly and completely in the presence of cuprous chloride and hydrochloric acid. It appears, therefore, that the formation of chloroprene from butadiene and hydrogen chloride involves 1,4 addition followed by rearrangement.

Since chloroprene polymerizes spontaneously, even at room temperature, polymerization inhibitors such as catechol, hydroquinone, amines, and aromatic nitro compounds are added if it is to be stored before using. If as little as 0.1% of catechol is added to chloroprene, it will remain liquid for several months. Also, when chloroprene is distilled (b.p. 59.4°C .), a suitable inhibitor is added before distillation.

Chloroprene can be polymerized alone, in solvents or as an emulsion. When allowed to polymerize at room temperature, ex-

posed to a little air, it is completely polymerized to a non-plastic polymer in ten days. The non-plastic polymer is a resilient, elastic product which resembles vulcanized soft rubber and which is called μ -polychloroprene.¹ It has a tensile strength of approximately 2000 lbs. per sq. in., and an elongation of 800%. It does not dissolve in typical rubber solvents such as benzene and carbon tetrachloride, but it does swell in these solvents. It also resembles rubber in that a stretched, cooled (in liquid air) sample can be shattered to form fibrous fragments. (Compare p. 39.) The x-ray diffraction pattern of stretched μ -polychloroprene is a fiber diagram which indicates a crystalline structure. The identity period of 4.8 Å indicates a *trans* configuration of the polymer. In this respect, μ -polychloroprene resembles gutta percha rather than rubber which has a *cis* configuration. (See p. 131.)

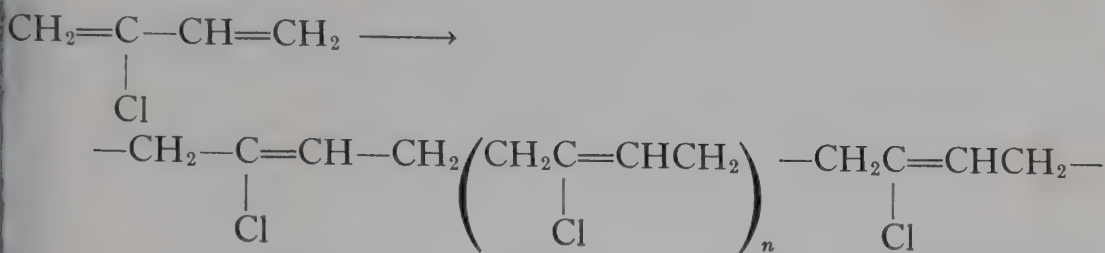
By polymerizing chloroprene at 60° C., in the absence of air, volatile, liquid polymers are obtained which resemble cyclic terpenes, and which have not yet achieved any importance. If polymerization is slow or is catalyzed by sodium or by light of wave length 3130 Å, then a granular polymer known as ω -polychloroprene is formed. The form is non-plastic, does not swell appreciably in solvents, is amorphous and of no commercial value.

The most important form of polychloroprene is the α -polymer. This product can be obtained by the partial polymerization of chloroprene. For example, if chloroprene is exposed to a 150-watt Mazda lamp for 16–24 hours at about 35° C., approximately 30% of the chloroprene will be polymerized. The viscous solution is poured into alcohol and the α -polychloroprene precipitates. This polymer is plastic, completely soluble in benzene, and resembles milled, unvulcanized rubber. On standing, it loses its plastic properties and changes to the insoluble, elastic μ -polychloroprene. The transformation occurs in 48 hours at 30° C.; in 5 minutes at 130° C. This change can be accelerated by the addition of zinc oxide, magnesium oxide, aniline or naphthylamines. Phenyl β -naphthylamine is a powerful inhibitor of this transformation of the α -polymer to the μ -polymer.

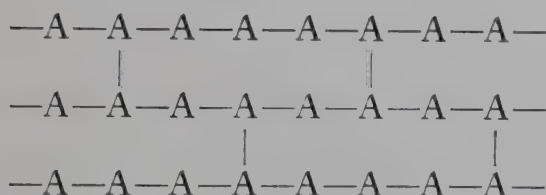
Since the changes in the physical properties resulting from the transformation of α -polychloroprene to μ -polychloroprene resemble those occurring when rubber is vulcanized (p. 143), the structures of these polymers should be considered. The α -polymer possesses the characteristics of a linear polymer and its formation can be repre-

¹ Carothers, Williams, Collins and Kirby, *J. Am. Chem. Soc.* **53**, 4203 (1931).

sented as follows:



The μ -polymer exhibits the characteristics of a cross-linked polymer and may have the following type of formula:

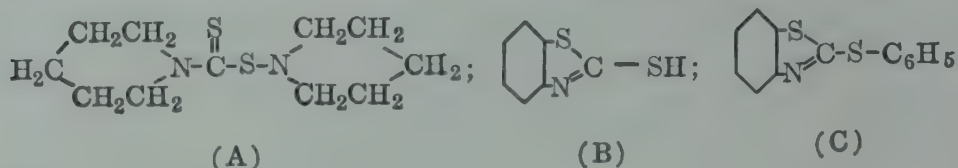


where A represents a chloroprene residue.

In view of the fact that α -polychloroprene can be milled and compounded before being cured or changed to the μ -polychloroprene, it is obviously desirable to have methods of controlling the polymerization and to find substances which can be added to the α -polymer to prevent it from changing to the μ -polymer either during milling or when stored for reasonably long periods of time. Among the numerous chemicals which have been described in the patent literature as being suitable for controlling the polymerization of chloroprene to give a good yield (80–90% in some cases) of the α -polymer are: phenols, aliphatic and aromatic amines, quinones, aromatic nitro compounds, iodine, bromine, hydrogen sulfide, either with or without elementary sulfur, organic sulfur compounds such as aliphatic and aromatic mercaptans, aromatic sulfinic acids, mercapto-carboxylic acids, (e.g., thioglycolic acid), tetraalkyl thiuram disulfides and diaryl dialkyl thiuram disulfides. These modifying agents are used in amounts varying from 0.125% to 2%.

Since emulsion polymerization of chloroprene is approximately twenty times as rapid as mass polymerization, the polymerization is usually carried out with emulsions of chloroprene and the modifying agent. The emulsion can be obtained with a soap such as sodium oleate or a wetting agent such as sodium stearyl sulfate, or it can be obtained in an acidic medium (pH 1–5) using cetyl trimethylammonium bromide as the emulsifying agent. A product with superior plastic properties is claimed for the emulsion polymerization in the

acidic medium. Polymerization is usually done at temperatures ranging from 20 to 40° C. for periods varying from one to forty-eight hours, shorter periods of time being used for the higher temperatures. As soon as possible after polymerization is complete, an emulsified solution (usually 1–2%) of a suitable inhibitor of μ -polymerization is added. Some of the most effective inhibitors are phenyl β -naphthylamine, trinitrobenzene, piperidine pentamethylene dithiocarbamate (A), mercaptobenzothiazole (B), phenyl benzothiazyl sulfide (C).



Coagulation of the polymer can be accomplished by pouring the emulsion into alcohol or by adding solid sodium chloride with vigorous agitation. After washing thoroughly, the polymer is ready for compounding and curing. Figure 19.1 shows Neoprene obtained from emulsion polymerization.

One formula for obtaining a pure gum compound of Neoprene is as follows:

Neoprene	100 parts
Magnesium oxide	10 "
Wood rosin	5 "
Zinc oxide	5 "

The magnesium oxide is usually added during the first part of the milling process (Figure 19.2) and the zinc oxide is added at the end of the compounding operation. Zinc oxide is added last, because it acts as a rapid accelerator and if added at the beginning of the milling process, might cause premature curing. Too much zinc oxide may cause scorching of the rubber during vulcanization. Magnesium oxide acts as a retarding agent for the vulcanization of most types, thus preventing scorching. It also causes an increase in the tensile strength of the Neoprene and serves to neutralize any traces of hydrogen chloride which may be formed by the photochemical decomposition of Neoprene. The rosin serves as a softening agent and is added in liquid form or frequently as a solution in cottonseed oil. Tricresyl phosphate is an excellent softener for the milling of Neoprene. Sulfur is often added as a catalyst for the vulcanization.

The nature and amount of other compounding agents will vary according to the properties desired in the final product. For example,

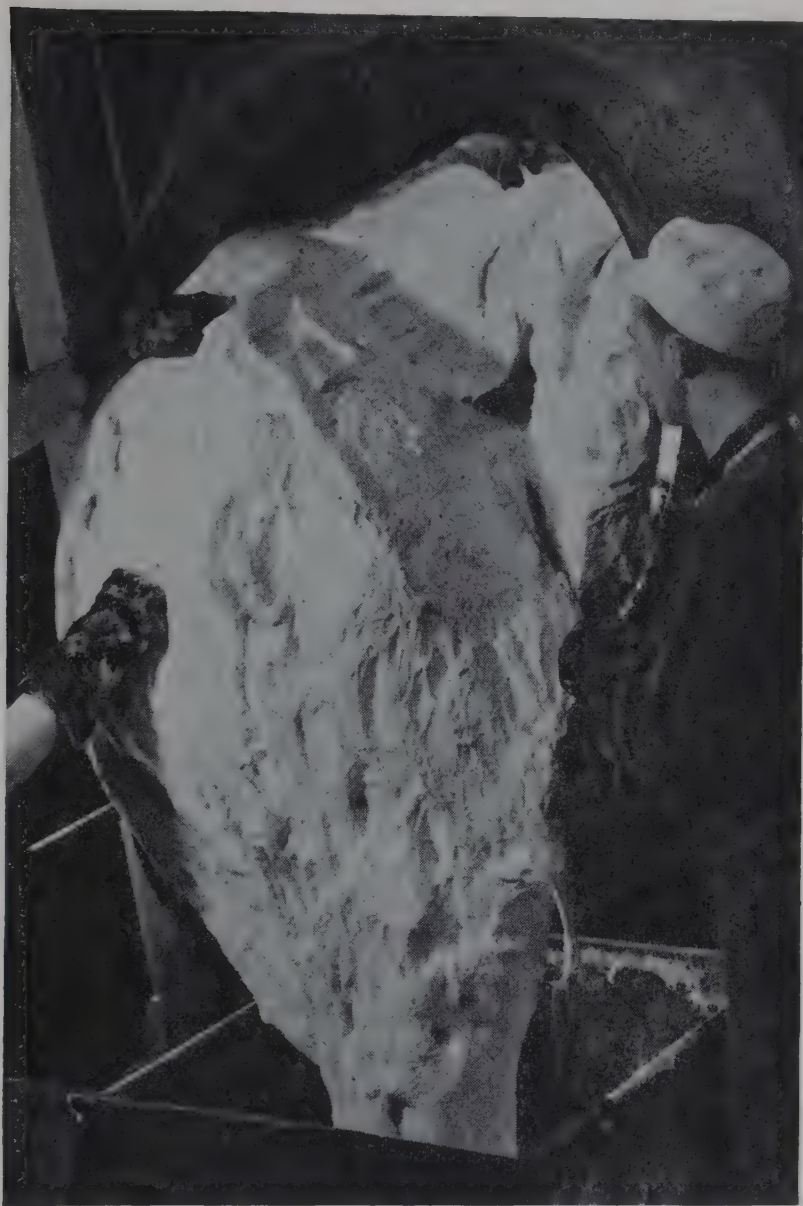


FIG. 19.1. Neoprene is being poured from polymerization kettles, after emulsion polymerization, followed by coagulation and decantation. (Courtesy Du Pont Company.)

when making a Neoprene compound to be used where oil resistance is necessary, a high proportion of a "medium" or "soft" carbon black is recommended, and sulfur must be included in the compounding. Oil resistance can also be obtained by incorporating up to 30% of a Thiokol type of elastomer made from glycerol dichlorohydrin and sodium polysulfide. If a heat-resistant Neoprene is desired, a "soft" carbon black should be used and sulfur should not be included in the formula. When hardness and resistance to abrasion are desired, a



FIG. 19.2. Milling of neoprene. (Courtesy of Du Pont Company.)

“hard” channel-type carbon black is used. An electrically resistant Neoprene should not contain more than 5% of a semi-reinforcing carbon black, and a D. C. resistivity of 1.2×10^{13} ohm-cm. has been obtained with a properly compounded and cured sample of Neoprene. On the other hand, a sample of Neoprene compounded with 50 parts of acetylene black (to 100 parts of Neoprene) and other ingredients showed a D. C. resistivity of 1.4×10^2 ohm-cm. A similarly compounded Neoprene, except that no carbon was added, had a D. C. resistivity of 1×10^{12} ohm-cm.²

Neoprene stocks can be softened by the addition of plasticizers or softeners such as dibutyl sebacate, dibutyl phthalate and various

² Yerzley, *Ind. Eng. Chem.* **35**, 330 (1943).

petroleum products. These softeners lower the temperature at which the Neoprene becomes brittle and hence are extremely valuable in making a product for use in cold climates.

The curing or vulcanizing of compounded Neoprenes is usually carried out at 130–140° C. for twenty to sixty minutes. The time and temperature of curing are important factors in determining the properties of the final product. Higher temperatures and longer periods of heating result in the formation of harder, more resistant products.

From the above observations it is evident that wide variations in properties are possible by

- (1) varying the rate and extent of polymerization with the aid of different modifying agents.
- (2) varying the nature of the inhibitor of the transformation of α -polymer to μ -polymer.
- (3) varying the nature and amount of the compounding ingredients, especially the kind and amount of carbon black,
- (4) varying the conditions of curing,
- (5) varying the nature and the amount of co-monomer in copolymerizations of chloroprene with such monomers as vinylidene dichloride, styrene, and acrylonitrile.

In its properties, Neoprene is particularly noted for its resistance to chemicals and oils, light, heat, and deterioration on aging. The

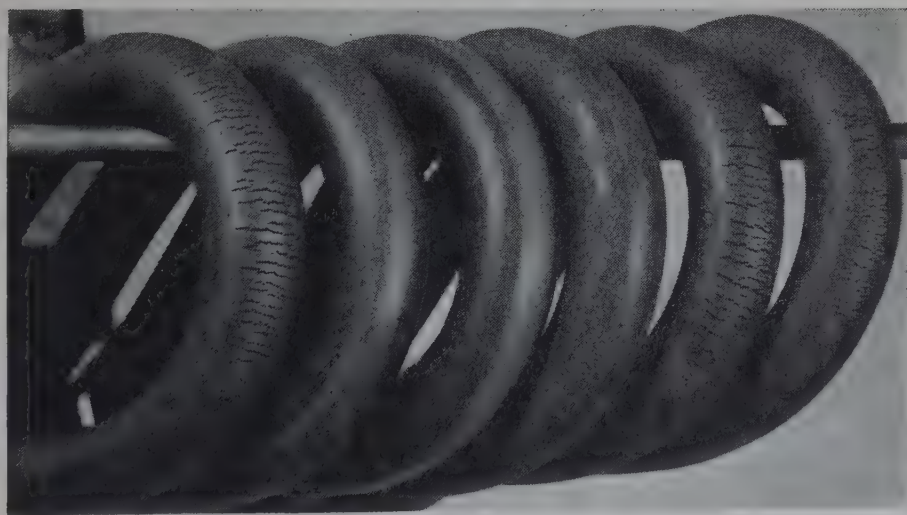


FIG. 19.3. Hose, subjected to a flexing test under Florida sun, shows superiority of three neoprene covered pieces, second, third and fourth from left, as compared to the rubber covered hoses, at extreme left, and two on the right. (Courtesy of Du Pont Company.)

superiority of Neoprene over natural rubber with respect to flexing in sunlight is illustrated in Figure 19.3. The superior resistance of Neoprene to the action of oil and grease is shown in Figure 19.4. Neoprene is characterized by a high modulus of elasticity, excellent elasticity and resiliency, and high tensile strength when properly compounded. Such a combination of properties makes Neoprene adaptable to such a variety of applications as conveyor belts, oil hoses, coated fabrics, printer's rolls, gaskets, shoe parts, gloves, cable coatings, fuel cells, tires and inner tubes.



FIG. 19.4. Oil and grease, which came in frequent contact with this pair of test boots, have not affected the one on the left, which is made of Neoprene, but have deteriorated the rubber sole of the boot at the right. (Courtesy of Du Pont Company.)

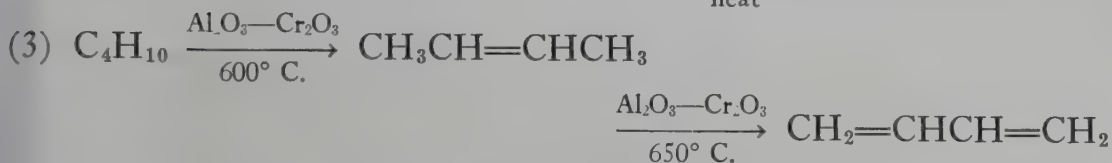
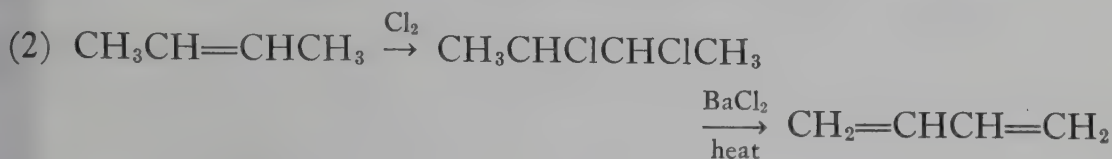
BUNA RUBBERS OR ELASTOMERS

The first type of Buna elastomer was formed from butadiene by polymerization in the presence of metallic sodium as a catalyst. Since the Buna elastomers have achieved a high degree of importance, polymerized butadiene being the principal synthetic rubber used in Russia at the present time, it is worth while to look briefly at some of the methods by which butadiene can be prepared. The raw

materials which are used can be grouped into three classes, namely, petroleum, carbohydrates and calcium carbide.

The three principal methods of making butadiene from petroleum which have been used on a commercial scale in this country are:³

(1) Special cracking of petroleum to yield 5-12% of butadiene

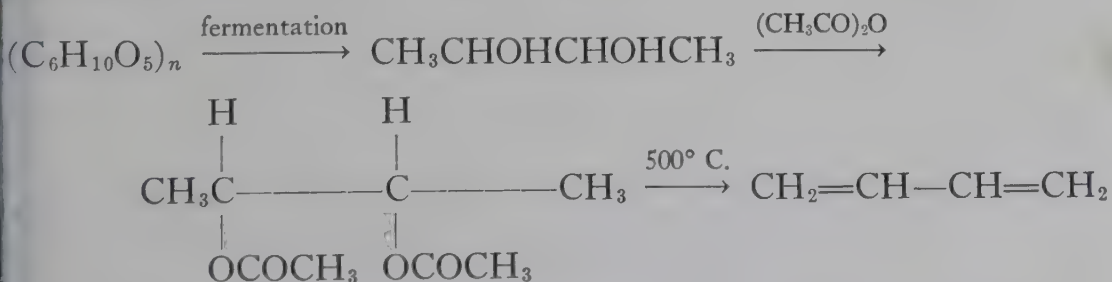


The 2-butene and *n*-butane are both obtained from the cracking of petroleum.

At present, the most important method of making butadiene from carbohydrates consists in fermenting the carbohydrate to form ethyl alcohol and then passing the alcohol vapor over a suitable catalyst at an elevated temperature. One catalyst that has been used is a mixture of aluminum oxide and zinc oxide.⁴ While an equation can be written for the reaction,



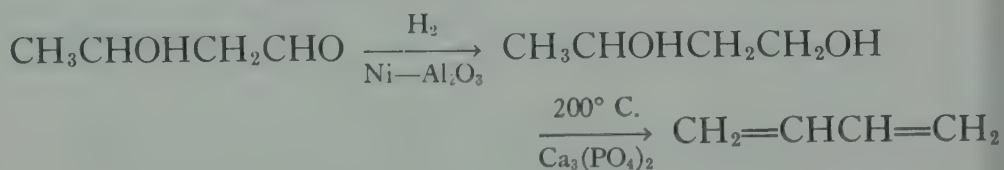
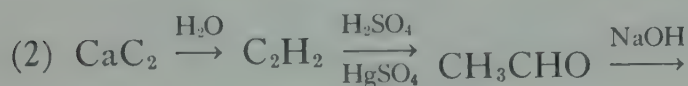
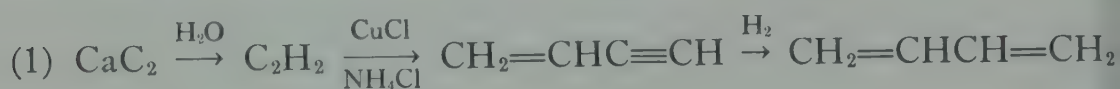
there are several by-products such as ethylene, butylene, acetaldehyde, ether, etc., which are formed simultaneously. A second method of making butadiene from carbohydrates consists in fermenting the carbohydrate to form 2,3-butylene glycol. Acetylation of this glycol followed by pyrolysis of the diacetate at 500° C. gives a good yield of butadiene. The chemical changes involved are represented by the following reactions:



³ Cramer, *Ind. Eng. Chem.* **34**, 245 (1942).

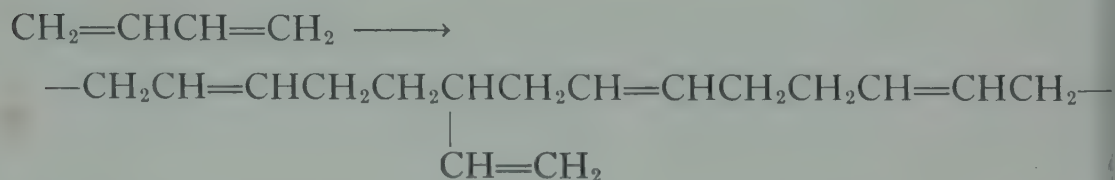
⁴ Elder, *Ind. Eng. Chem.* **34**, 1262 (1942).

There are two methods of making butadiene from calcium carbide and they are represented by the following reactions:



The sodium catalyst for the polymerization of butadiene may be made by dipping clean wire rods into molten sodium and immediately coating the solidified sodium with a layer of paraffin wax to prevent it from oxidizing or reacting with the moisture of the atmosphere. These rods are immersed in liquid butadiene in an autoclave under pressure and the polymerization is carried out at 50° C. Once started, the reaction is exothermic and the autoclave must be cooled in order to maintain the desired temperature. According to Naunton,⁵ three to eight days are required for the polymerization. About 0.5% of sodium is used, based upon the weight of synthetic rubber produced. A newer method, developed in Russia, consists in passing gaseous butadiene over screens coated with sodium sand gels. Although little information is yet available on this process, it is believed that a more uniform product of superior quality is obtained. Butadiene can also be polymerized by means of an emulsion technique.

Chain growth of the polymer occurs as a result of both 1,4 and 1,2 addition, with 1,4 addition predominating, e.g.



The occasional vinyl groups (resulting from 1,2 addition) linked to the chain may become involved in the formation of another chain with consequent cross-linking between two or more chains.

⁵ Naunton, *Synthetic Rubber*, p. 44, MacMillan and Company, Ltd., London, England (1937).

However, polymers of butadiene alone are not used in this country, for the reason that copolymers, especially copolymers with styrene or acrylonitrile, are definitely superior, for all purposes, to polymerized butadiene. In the manufacture of these copolymers, developments in the technique of emulsion polymerization have led to the utilization of this method as preferable to the mass polymerization in which sodium is used as the catalyst.

In this emulsion polymerization, the styrene or acrylonitrile is emulsified with sodium oleate or other suitable emulsifying agent. Acidic emulsifying agents such as an aqueous solution of diethylaminoethyloleamide hydrochloride containing a small amount of trichloroacetic acid may be used. Either inorganic or organic peroxides are added to act as catalysts for the polymerization. Modifying agents such as alkyl polyhalides and organic sulfur compounds, especially long chain mercaptans, are added. These chemicals are believed to promote 1,4-addition of the butadiene, thereby preventing branching and cross-linking, and are also believed to control the extent of polymerization. Butadiene is then introduced into the autoclave under pressure, the reaction mixture is well agitated and the polymerization is carried out, usually at a temperature of 40–60° C. for a period of 10–15 hours. In order to prevent a continuation of the polymerization with the resultant formation of a hard polymer which would be difficult to mill, an inhibitor such as phenyl β -naphthylamine is added, usually in emulsified form, when the polymerization has reached the desired stage. The polymer may then be coagulated by the addition of acid, washed and dried.

The physical conditions of temperature, pressure and concentration, under which the emulsion polymerization is carried out, the nature of the emulsifying agent, the nature and the amount of the catalysts and modifying agents, all have an effect on the amounts of linear, branched and cross-linked polymer molecules formed. The ratio of the monomers used will also have an effect on the properties of the final product. It is thus found that broadly variable properties of solubility, strength and heat sensitivity result from changes in the polymerization procedure. Although emulsion polymerizations were originally carried out as batch processes, methods for the continuous production of emulsion polymers have been developed.⁶

When styrene is used as the co-monomer, the product is known

⁶ British Patent 517,951 (1940).

as Buna S; when acrylonitrile is copolymerized with butadiene, the product is Buna N. Further designation of these products is often necessary because of variation of the monomer ratios. Thus, Perbunan and Perbunan Extra designate Buna N types with different proportions of acrylonitrile. Likewise HyCar OR 5, 15, and 25 indicate different polymeric types obtained from the same starting ingredients. The properties of such macromolecules may be indicated only in general terms, therefore, because of the variability of special derivatives. Each class is discussed individually.

The Buna S elastomers were chosen as the principal type in the Government's program (World War II) of producing synthetic rubbers. Most rubber technologists consider it as the type most similar to natural rubber in its processing and performance. The most widely used Buna S is one which is made from a mixture of 75% butadiene and 25% styrene.

During the milling of the copolymer, softening agents such as stearic acid, coal tar or pine tar are added in amounts varying from 1.5–3%. As in the case of natural rubber, sulfur (1.75–2.25%), vulcanization accelerators, preferably of the thiazole type, antioxidants and zinc oxide (2–5%) are compounded into the copolymer during milling. The incorporation of carbon blacks into Buna S is even more important and produces a greater effect than when natural rubber is used because the tensile strength of pure gum stock of Buna S is much lower than that of pure gum stock obtained from natural rubber. Buna S elastomers are especially valuable because of their excellent electrical characteristics, resistance to light and aging deterioration in air, retention of strength when optimum vulcanization time is exceeded, heat resistance, and abrasion resistance. The latter property is generally considered as superior to that of natural rubber. However, the fact that Buna S has lower tear resistance and lower flex life than natural rubber makes it less desirable when abrasion resistance is sought in a commercial product. No excessive oil resistance is claimed for the Buna S type because its solubility is comparable to that of natural rubber. When proper processing methods are applied or when the polymerization is regulated to production of a chain polymer, solubility in petroleum solvents results. Buna S is useful for the manufacture of automobile tires, coated fabrics, tubing, cable coatings and machine mountings. A synthetic rubber which is claimed to be superior to Buna S with respect to oil resistance, water resistance, tensile strength when hot,

and resistance to heat aging, is obtained by the copolymerization of butadiene with dichlorostyrene.⁷

The Buna N elastomers are similar to the Buna S types in their ability to be vulcanized by the usual sulfur and accelerator agents.

The lower degree of unsaturation in the Buna copolymers as compared to natural rubber permits a decrease in the amounts of sulfur and accelerator. In Buna N, satisfactory results are obtained by the use of 2% sulfur, based on the amount of Buna N used. The accelerator content is determined to a large extent by the filler, because retardation or advancement of the cure may result from a change of filler. A basic formulation for the compounding of Buna N is represented by the following:

Buna N	100 parts
Stearic acid	1 part
Coal tar or	
Ester plasticizer	15 parts
Zinc oxide	5 parts
Sulfur	2 parts
Benzothiazyl disulfide	1 part
Reinforcing carbon	50-75 parts

Because of their low degree of plasticity and greater resistance to breakdown procedures, more general use of plasticizing agents—particularly oxygenated derivatives—is required in the processing of these elastomers. The same types of fillers and reinforcing agents that are used with natural rubber may be incorporated into these synthetic rubbers. The use of semi-reinforcing carbon blacks is particularly recommended. Similarity to the Buna S derivatives is evident during vulcanization by the fact that the characteristics of strength and elasticity are well retained with over-vulcanization. Other properties of importance include their heat resistance, range of tensile strengths and elongations, excellent abrasion resistance, ability to withstand light and aging conditions, and particularly their oil resistance. In such characteristics as tear resistance, rebound and hysteresis factors, the performance, however, is inferior to that of natural rubber. It may be concluded that for special purposes such as oil or ozone resistance the Buna N synthetic rubbers are of special importance whereas in general characteristics of strength, elasticity, and flexing, no advantages over natural rubber are ob-

⁷ Michalek and Clark, *Chem. and Eng. News*, 22, 1561 (1944).



FIG. 19.5. Fuel cell, built to fit inside the wing or fuselage of an airplane. (A) is a strong outside wall of synthetic rubber and fabric. (B) is the sticky sealing material made from such gasoline sensitive substances as natural rubber or Buna S. (C) is the inner lining of specially compounded, gasoline-resisting, synthetic rubber such as Buna N. (Courtesy of United States Rubber Company.)

tained. Application of these derivatives to gaskets, fuel tanks, shoe soles, tires, fabrics, and adhesive cements has demonstrated their usefulness. Figures 19.5, 19.6 and 19.7 illustrate the principles involved in the use of self-sealing fuel tanks.

BUTYL RUBBER

The investigation which led to the development of Butyl rubber started with the polymerization of isobutylene to form a rubber-like

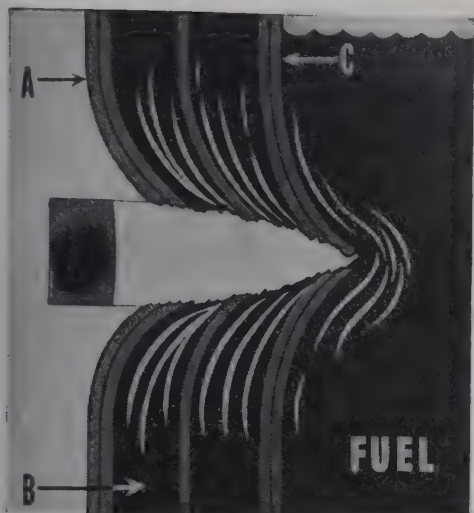


FIG. 19.6. When the bullet penetrates the outside wall of the fuel cell (A), the layer of sticky, elastic sealing material (B) surrounds the bullet. The sealant springs together quickly and closes the hole as the bullet passes through. (Courtesy of United States Rubber Company.)

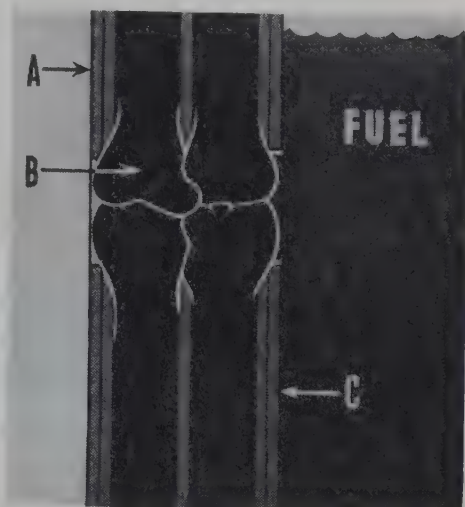


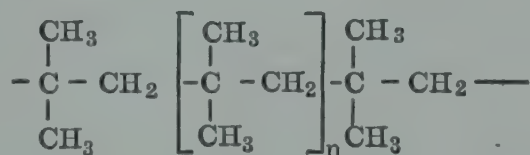
FIG. 19.7. Some of the fuel touches the sealant (B) and makes it swell, completing the seal. (Courtesy of United States Rubber Company.)

saturated hydrocarbon. The fact that isobutylene can be polymerized (mass polymerization) when treated with boron fluoride, sulfuric acid or anhydrous aluminum chloride at a low temperature has been known for a long time. Until recently, the polymers formed were liquids, having molecular weights varying from 2000 to 25,000. These liquids have been found to be valuable in improving the viscosity index of lubricating oils, and the penetration and aging characteristics of asphalts. Recently, however, it was discovered that higher molecular weight polymers which are elastic solids could be obtained. The change from a viscous liquid to an elastic solid occurs when the molecular weight reaches about 27,000. Solid polymers with molecular weights up to 400,000 have been prepared. The polymerization can also be performed in the presence of solvents such as liquid propane, liquid butane, liquid ethane, liquid ethylene or mixtures of these liquids. As in other polymerizations, the lower the temperature, the higher the molecular weights of the polymers formed. In order to control the molecular weight, small amounts ($< 1\%$) of mercaptans, di- and poly-sulfides, hydrogen sulfide or sulfur may be added. Larger amounts (10–25%) of *n*-butylene and propylene also act as inhibitors to prevent the formation of too high

molecular weight products. In a typical case,⁸ the addition of 0.15% of a low boiling mercaptan to the polymerizing mixture yielded a polymer having approximately one-third the molecular weight of the polymer produced when no mercaptan was added and the other experimental conditions were the same.

The solid polymers are saturated and, therefore, non-vulcanizable. The saturated character is responsible for many of their properties such as resistance to chemicals, ozone, ultra-violet light and aging. They possess excellent electrical properties, poor rebound and are subject to cold flow. The solid polymers are used to improve the quality of greases and lubricating oils, and, when added to wax, they increase the viscosity and decrease the tendency of the wax to become brittle at low temperatures. Polymers treated with a small amount of sulfur monochloride are useful in making extreme pressure lubricants.

One of the difficulties in the adaptation of polyisobutylene to the fabrication of rubber-like articles is the fact that it is not worked or milled easily. A consideration of the probable formula for polyisobutylene (or polybutene as it is generally called) shows that it is a saturated molecule, e.g.,



It was thought that the introduction of some unsaturation into the polymer might yield a product that could be milled more satisfactorily and could be vulcanized. These desirable results were achieved by the addition of a small amount (approx. 2%) of a diolefine such as isoprene or butadiene to the isobutylene. The amount of diolefine added is such that the unsaturation of the polymer will be 0.7–3.0% of that of natural rubber. The products are known as Butyl rubbers or elastomers.

This reaction may be carried out by dissolving the mixture of monomers in liquid ethylene at a temperature of -98°C . A suitable catalyst consists of 0.5 part of anhydrous aluminum chloride dissolved in 100 parts of methyl chloride, cooled to -78°C . When the catalyst solution is sprayed onto the surface of the reaction mixture, polymerization occurs rapidly, with the formation of a white precipitate. When all of the catalyst has been added, the

⁸ Otto and Schneider, U. S. Patent 2,172,403 (1939).

polymerization ceases. The residual catalyst is destroyed by adding a small amount of oxygenated organic compound such as methyl or ethyl alcohol or an alkaline substance such as ammonia or sodium carbonate solution. After separation of the polymer and warming to room temperature the material is washed to remove catalyst, unpolymerized olefines, and diluent-refrigerant.

Since there is not a great deal of breakdown during milling, the properties of the final product are controlled, to a considerable extent, by the copolymer.⁹ For example, Butyl rubber is vulcanized or cured more slowly than natural rubber. However, by increasing the amount of unsaturation, the rate of curing can be increased. Furthermore, the more unsaturated the copolymer, the greater the modulus of elasticity and the greater the rebound. With an increase in the molecular weight (unsaturation kept constant), there is an improvement in the tensile strength and the modulus of elasticity. Increasing the molecular weight has practically no effect on the rebound, which is very much lower than that of natural rubber at room temperature, though only a little inferior to natural rubber at 100° C. Both the rebound and the plasticity of Butyl rubber can be improved by the addition of small amounts of elasticators such as dibenzyl ether, ethyl biphenyl ether and *p*-cymene.

For the vulcanization of Butyl rubber, ultra-accelerators such as tetramethylthiuram disulfide (1.25–1.5%) are used, sometimes with a thiazole such as mercaptobenzothiazole (0.5–0.6%) to supplement the accelerator. Selenium diethyldithiocarbamate (Selenac) may also be added in small amounts (1.25%). A novel method of vulcanizing butyl rubber which was widely used when it was first introduced involves heating it with a mixture of lead dioxide and *p*-benzoquinone dioxime.

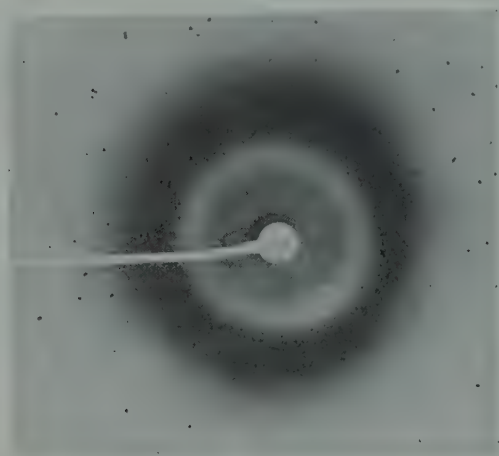
The addition of carbon black to Butyl rubber does not furnish any marked improvement in the tensile strength. This is in distinct contrast to the substantial improvement in the tensile strength of natural rubber containing carbon black over that of the pure gum stock. However, the addition of carbon black to butyl rubber does improve its abrasion resistance, tear resistance and modulus of elasticity.

Butyl rubber is inferior to natural rubber with respect to tensile strength, tear resistance and rebound characteristics. It is also more soluble in petroleum hydrocarbons, though it is resistant to many vegetable and animal oils. On the other hand, it is superior

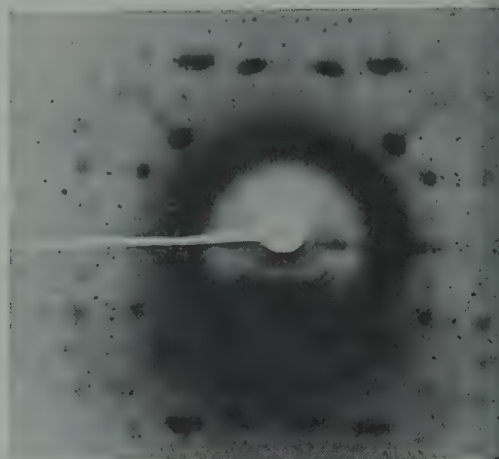
⁹ Haworth and Baldwin, *Ind. Eng. Chem.* **34**, 1301 (1942).

to natural rubber with respect to flex life, electrical properties, impermeability to gases, resistance to acids, alkalies, moisture, ozone and aging.

The X-ray diagrams of unstretched and stretched Butyl rubber are comparable to those of natural rubber in that the unstretched form shows a typical amorphous pattern (Figure 19.8A) while the stretched rubber (Figure 19.8B) shows definite evidence of crystallinity.



A



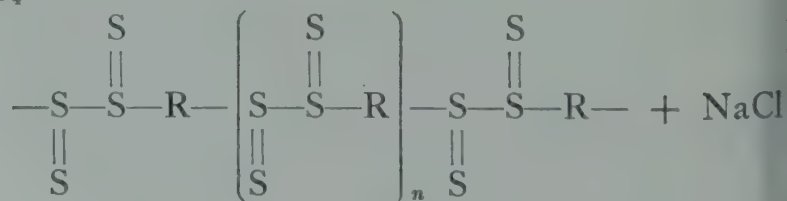
B

FIG. 19.8. X-Ray diagrams of unstretched (A) and stretched (B) Butyl elastomer. (Courtesy of Esso Laboratories of the Standard Oil Development Company.)

Butyl rubber is used to make chemical tubing, insulation, gas-resistant clothing, rubberized fabric for hospital sheeting, and caulking compounds.

THIOKOL

No synthetic rubber differs more from the polyisoprene structure of natural rubber than the Thiokol derivatives. The structure is fundamentally that of a polysulfide resulting from the condensation reaction of a dihalide with sodium tetrasulfide. The general reaction,

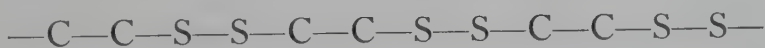


represents the changes involved. The radical represented by R may be varied to effect changes in the properties of the synthetic rubber formed. The two halides which are most widely used are ethylene dichloride and 2,2'-dichlorodiethyl ether (Chlorex). The polymer¹⁰ obtained from ethylene dichloride and sodium tetrasulfide is known as Thiokol A while that obtained when 2,2'-dichlorodiethyl ether is used is called Thiokol B. Other polyhalides used include dichloroethyl formal, $\text{H}_2\text{C}(\text{OCH}_2\text{CH}_2\text{Cl})_2$, used in making Thiokol FA and a mixture of dichloroethyl formal and trichloropropane, used in making Thiokol ST.

There is considerable evidence to indicate that these polymers are tetrasulfides. In the first place, the percentage of sulfur in Thiokol A is the same as that which would be expected in a compound having the formula $(\text{C}_2\text{H}_4\text{S}_4)_n$, namely 82%. If the ethylene tetrasulfide polymer is heated with sodium hydroxide solution, a polymeric ethylene disulfide is obtained which is identical with that formed by the oxidation of ethylene mercaptan.



Furthermore, one mole of this polymeric disulfide can be treated with two atomic equivalents of sulfur, milled, cooled and then heated to form a product which is identical with the original polymeric tetrasulfide. These data indicate that the polymeric chain consists of the skeleton

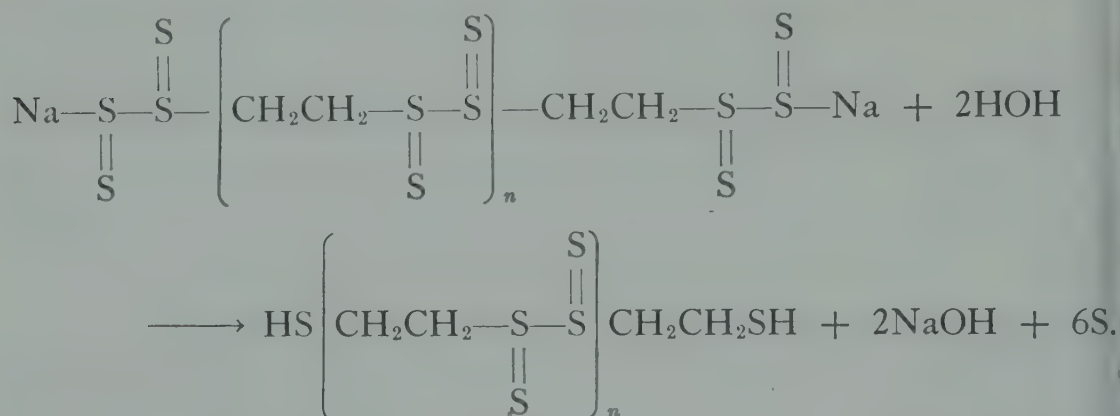


with one additional sulfur atom linked to each sulfur atom in the chain. X-ray data corroborate these conclusions based upon the chemical reactions and also indicate that the sulfur atoms have a *trans* arrangement as shown on p. 388. It is interesting to note that the polymeric disulfide obtained from Thiokol A does not have any rubbery characteristics, while that obtained from Thiokol B does possess rubber-like properties. This latter product is known as Thiokol D.

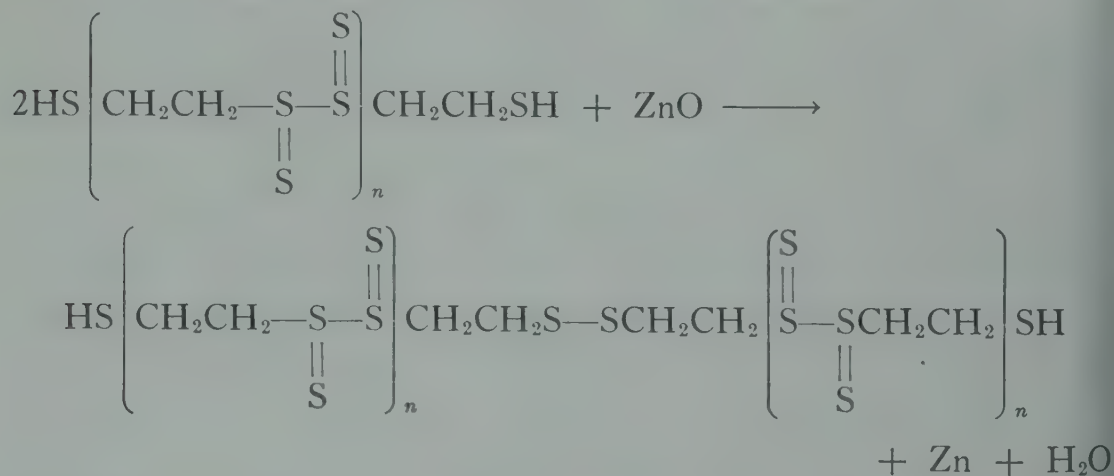
When the condensation polymerization is carried out using an excess of ethylene dichloride, the polymer is a viscous liquid and is believed to have terminal chlorine atoms. If an excess of sodium tetrasulfide is used, the product is rubber-like. In this case, it is believed that the terminal groups are mercaptan (SH) groups,

¹⁰ Martin and Patrick, *Ind. Eng. Chem.* **28**, 1145 (1936).

formed by the hydrolysis of the terminal polysulfide group, e.g.,



Some evidence for the existence of terminal mercaptan groups is found in the fact that the plastic condensation product can be vulcanized by heating it with metallic oxides or with organic oxidizing agents such as trinitrobenzene or peroxides. Although vulcanization of natural or synthetic rubber usually involves an increase in the molecular weight as a result of the formation of cross-linkages, it is probable, in the case of Thiokol, that the increased molecular weight is due to a lengthening of the polymeric chains, e.g.,



It is not clear how zinc oxide could react with the linear polymer to form any cross-linkages.

The compounding and processing of Thiokol polymers are similar to the corresponding procedures used with natural rubber. The addition of chemical plasticizing agents such as mercaptobenzothiazole, benzothiazyl disulfide and diphenylguanidine facilitate the softening of the polymer on the mill. About ten parts of zinc oxide for each hundred parts of Thiokol is milled into the polymer to serve as a

vulcanizing agent. Soft and semi-reinforcing carbon blacks are incorporated in order to develop maximum strength and toughness in the finished product. Vulcanization occurs when the compounded material is heated to 140°C .

The properties of the several Thiokols vary somewhat, depending on the nature of the dihalide used and whether the polymer is a tetrasulfide or a disulfide. In general, however, they exhibit good resistance to organic solvents. Type A is resistant to all organic solvents, while the others are not attacked by petroleum hydrocarbons, but are swelled by certain aromatic and chlorinated solvents. Thiokol B is the only type of Thiokol which is resistant to mustard gas and which can be applied by a spreading process. All Thiokols are stable to light and have excellent aging characteristics. Some Thiokols, particularly Thiokol FA, can be obtained in granular form and used as molding powders. Thiokols are inferior to natural rubber with respect to tensile strength, resiliency, resistance to cold flow, abrasion and temperature resistance, but superior in general resistance to chemicals. Thiokol is used in making fuel cells, chemical tubing or hose (Figure 19.9) for transporting oils and paints, printing rolls and electric cable coverings.

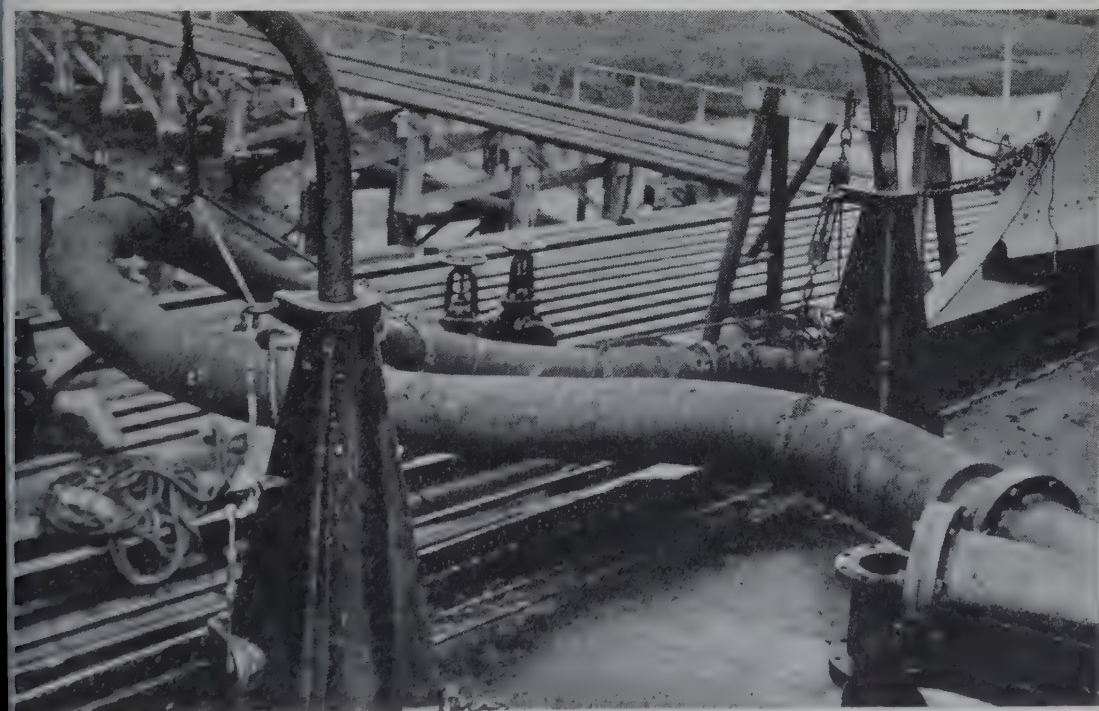


FIG. 19.9. Thiokol hose for conveying oil. (Courtesy of Thiokol Corporation.)

Review Questions

1. Compare the classical approach with the modern approach to the problem of producing a synthetic rubber.
2. Show by chemical formulas the relationship of the structures of natural rubber, Neoprene, Buna N, Buna S, and Butyl rubbers.
3. What types of synthetic rubber are produced by
 - (a) condensation polymerization
 - (b) simple addition polymerization
 - (c) copolymerization?
4. Describe in detail the production of:
 - (a) Buna S (sodium process)
 - (b) Buna N (emulsion process)
 - (c) Butyl rubber.
5. Describe the preparation and properties of:
 - (a) α -polychloroprene
 - (b) μ -polychloroprene.
6. Indicate the sources of butadiene and also the reactions by which it can be produced.
7. List the vulcanization ingredients used for the different types of synthetic rubbers.
8. State the outstanding physical properties of:
 - (a) Neoprene
 - (b) Buna S
 - (c) Buna N
 - (d) Thiokol
 - (e) Butyl rubber.
9. What are the ingredients used to produce
 - (a) Thiokol A
 - (b) Thiokol B
 - (c) Thiokol FA
 - (d) Thiokol ST?

What is the probable "vulcanization" reaction involved in the preparation of Thiokol?

10. What factors can be varied in order to produce different properties in Buna N synthetic rubbers?

SECTION III
FABRICATION

CHAPTER XX

COMPOUNDING

The discussion up to this point has been concerned chiefly with the variation of properties of plastics with changes in their chemical structures. The differences between the particular groups: Phenolics, Ureas, Celluloses, Vinyls, etc., have been pointed out and, furthermore, the changes which result from modification of the monomeric units used in polymerization have been mentioned. The chemical variations may be summarized as follows:

(a) Average molecular weight with its resultant effect on all properties from solubility to tensile strength.

(b) Polymerization technique and structural differences caused by its variation. The difference between one- and two-step phenolics is a typical example.

(c) Ratio of components when copolymerization is involved.

(d) Degree of substitution reaction when the plastic results from chemical modification of some other macromolecule. Changing polyvinyl acetate to polyvinyl acetal or cellulose to cellulose acetate results in different polymers according to the extent of the conversion reaction.

(e) The molecular weight and structure of the monomeric unit used. Thus, the esters of acrylic acid—methyl, ethyl, propyl, etc.—form an homologous series capable of producing an homologous series of plastic products. Each polymer differs from the others in characteristic properties, depending upon the monomer used.

This summation of chemical effects which cause variation of plastics properties makes it evident that the variability and choice of combinations is almost limitless. Although availability of raw materials or ease of manufacture often makes one type more attractive than similar ones, generalization of properties to any class of plastics is difficult.

The problem of stating general characteristics which may be applied to all members of a family of plastics is made even more difficult by the fact that mechanical compounding and incorporation of modifying agents may often alter the original properties beyond recognition. Even the association of specific properties with a

specific plastic is well-nigh impossible. The subject may, however, be discussed in broad terms and various properties may be correlated with certain compounding agents. In this way, a foundation for prediction may be established. In effect, the art of compounding has arisen principally as a consequence of two desires. First, basic properties may be either modified or enhanced and, secondly, the fabrication of the resultant mix may be made easier by selection of the proper ingredients.

A typical molding powder was previously described (Chapter VII) as consisting of:

Base Resin
Filler
Plasticizer
Lubricant
Dye or Pigment,

mixed in desired proportions for realization of optimum properties. When the service requisites are outlined and the manufacturing limitations are known, the proper formula may be determined. It will be found, in general, that the filler is the chief compounding constituent with the resin when a thermosetting type is involved, while, with a thermoplastic resin, the plasticizer becomes of greatest importance. Fillers in the former case modify properties to an appreciable extent and are in consequence carefully selected. In the case of thermoplastics, however, they rarely serve any purpose other than that of cheapening the base resin. When a plasticizer is used with most thermoplastics, the characteristics of resiliency and flexibility are improved and consequently the toughness is increased. Plasticizers are less frequently used with the thermosetting types, but small amounts of plasticizer have the effect of materially improving the ease of fabrication in the production of intricately designed objects. Fillers, of course, also extend thermosetting resins, and plasticizers increase the bulk of thermoplastics, but these changes are less obvious than those mentioned above. The functions of each compounding agent will be discussed in some detail.

FILLERS

The amounts of this compounding agent used with any resin, but particularly with phenolics, may be varied from small to predominant proportions. Fundamental characteristics are associated with each type used, and the filler is often mentioned in the naming of a plastic base; e.g., mica filled phenolics, asbestos filled phenolics.

Fundamentally, the fillers may be subdivided into two groups: organic, e.g., cellulosic materials, and inorganic, e.g., metallic salts and silicates.

The properties which are sought in a filler and the standards by which they may be judged include:

- (a) Low cost and abundant supply.
- (b) Compatibility and ease of mixing with resins and dyes.
- (c) Low moisture absorption.
- (d) High mechanical strength.
- (e) Ease of molding and pre-forming of molding powder.
- (f) High heat resistance.
- (g) Favorable electrical characteristics.
- (h) Absence of abrasive or chemical effects on the mold.

Figure 20.1, p. 400, represents the rather wide variations of properties obtainable by the use of different fillers in a phenol-formaldehyde resin. Although numerical values are not given, their widely varying effect on various properties is apparent from an examination of the chart. The height of the bar indicates the desirability of the property. For example, even though the specific gravity of a wood flour filled phenolic resin is low, the bar is relatively high, indicating that a low specific gravity is commercially desirable because more pieces per pound are obtained. To serve as a guide in studying the charts, the actual numerical property values of a typical wood flour-filled Resinox molding compound are listed at the top of each column.

Wood Flour.—The most widely used filler for all-purpose versatility, particularly in the case of phenolics, is wood flour. The requirements of the product usually involve the use of light-colored woods such as pine, spruce, fir, and poplar although the hard, darker woods of maple, birch and oak have been used. The material used is first separated from bark and knots, the moisture content adjusted (2–3%), and, finally, the wood is ground to desired mesh size. The latter process is of considerable importance. So-called *attrition* grinding tends to separate the fibers in a more or less undamaged condition in spite of the fact that grinding to a fine mesh size is carried out.

Much of the advantage of wood flour stems from the fact that it has a low specific gravity. Its value in extending the resin is due to the greater volume of molded products formed per pound of base. The general characteristics, also, are favorable to its widespread application. Excellent moldability, good shock resistance, high

tensile strength, good electrical characteristics, adaptability to machining, and low heat conductivity are typical properties of resinous products containing wood flour. There are, however, some drawbacks in the general application of wood flour. In many cases, the properties listed above are not high enough for special purposes; in other instances the shrinkage in service, moisture absorption, or relatively low temperature resistance (135°C.), prevent its use. Such substitutes as hempherds, soybean meal, seed hulls and paper pulp have been suggested as replacements for wood flour. A special grade of cellulose known as alpha cellulose is used in conjunction with ureas because of its value in imparting translucency and colorability.

Cotton and Other Textile Fillers.—The use of cotton flock or finely ground cotton as a filler is particularly recommended where high strength is desired. When such factors as tensile, impact and flexural strengths are of importance to the service of the molded piece, use of properly prepared cotton flock is advised. Likewise, such an assorted array of fabric scrap as shearings, rags, and clippings may be bleached, purified and shredded for use as fillers for molded objects. This type of filler, generally classified as shredded textiles, or simply, fabric filler, imparts maximum mechanical strength, first, because of its fibrous nature, and secondly, due to the fact that much of the original spinning and cross-linking of the fibers is retained. Such products as gears, machine housings, and rayon spinning buckets may be readily fabricated to meet strength specifications when fabric filler is used.

Associated with the desirable characteristics, however, there are certain factors which limit the use of fabric fillers. For example, moisture absorption of the fabricated piece is high, machining operations are difficult because of the exposed fibers at the surface, and moldability is decreased because of the high bulk ratio of the molding powder.

Asbestos.—This is probably the most widely-used mineral filler in the plastics industry for it imparts the typical characteristics of mineral fillers without excessive loss of strength. This is undoubtedly due to the fibrous structure of the filler. Thus, such factors as flow in the mold, dimensional stability, minimum after-shrinkage, exceptionally low moisture absorption, and good electrical properties are exhibited at some sacrifice in strength as compared with the fabric fillers. The composition of the filler is that of hydrated magnesium silicate and in its physical form, it consists of fine fibers admixed with considerable dust and non-fibrous material.

Of greatest importance in the fabrication of plastics employing asbestos is the exceptionally high heat resistance and its impermeability to moisture and chemicals. The former permits production of pieces which withstand temperatures of 204°C . (400°F .). The chemical and moisture resistance are responsible for wide acceptance of such phenolic-asbestos compositions as Haveg (p. 185). At the same time, the characteristic permanence of dimensions is accounted for in part by the low moisture absorption.

Caution must be exercised in the application of asbestos or other mineral fillers of similar nature. Greater abrasion of the mold, machining difficulties and surface color irregularities are caused by this filler. New developments, however, have led to improved grades and types of asbestos filler. Of particular interest are the newer types which produce high impact strength, and advances made in producing more favorable electrical properties.

Diatomaceous Silica.—This naturally-occurring material which consists fundamentally of pure silica associated with traces of the alkali metals, alkaline earths, alumina and iron oxide is used to obtain many of the properties described in connection with asbestos. The diatomaceous filler is controlled within narrow limits of mesh size, color, density, and moisture content. The general characteristics of high heat resistance, surface hardness, favorable electrical properties (low power factor), and moisture resistance are characteristic of the products formed. Some sacrifice of strength is again made, however, as brittleness is increased.

Mica.—The insulating value of mica is well known. Electrical applications involving the use of a plastic often require the addition of mica in the form of a finely-ground powder as a filler material. Chemically, the product is a complex combination of the acid silicates of aluminum and potassium. Excellent insulating properties and low power loss at high frequencies are characteristic of resins containing mica. Also, superior moisture resistance and heat resistance are introduced. The use of mica alone, however, often results in unfavorable brittleness and strength, particularly with higher proportions of filler. Under these conditions, peeling and sticking to the mold result. Fabric fillers are often used in combination with the mica in order to produce required shock resistance. The impact strengths of phenolic resins containing mica or fabric will be found in Figure 20.1, p. 400.

Graphite.—This filler is used in limited quantities because of its special lubrication value. The lubrication influence is evident during the molding operation where graphite permits ease of removal from



FIG. 20.1. Effect of various fillers upon physical properties. (Courtesy of Monsanto Chemical Company.)

the mold. When used in larger quantities, graphite introduces self-lubricating qualities into the product formed. Small bearings, for example, are often formed by the use of this filler. The resistance to acids is also improved by its use.

Miscellaneous Fillers.—The principal class of miscellaneous types are the metallic salts such as calcium carbonate, barium sulfate, zinc oxide and calcium sulfate. Although such types are more generally applied to rubber compounding, they are often used as fillers in plastics when special characteristics are desired. Acid resistance, low moisture absorption, high temperature resistance, hardness and low cost often favor their use.

In summary, Table I-20 represents the association of typical applications with representative fillers which might be used:

TABLE I-20. MOLDED PLASTICS AND RELATION OF FILLERS TO APPLICATIONS ^a

Resin Binder	Nature of Filler	Characteristics Displayed	Typical Examples
Phenol-formaldehyde	Wood flour (vacuum dried)	Excellent electrical qualities	Ignition coil housings
Phenol-formaldehyde	Wood flour	General characteristics	Housings for radios, closures for bottles
Urea-formaldehyde	Purified wood cellulose	Appearance—translucent	Housing for clocks, handles
Phenol-formaldehyde	Cotton fibers	Improved impact resistance, good surface appearance	Telephone handsets
Phenol-formaldehyde	Shredded fabric	High impact strength	Housings for drilling and grinding machines, gears, couplings
Phenol-formaldehyde	Graphite	Lubricating qualities	Self-lubricating bearings
Phenol-formaldehyde	Asbestos	Heat and chemical resistance	Brake linings, clutch facings, plugs
Phenol-formaldehyde	Mica	Low loss electrical properties	Coil housings, mechanical supports for radio parts

^a Del Monte, *Plastics in Engineering*, p. 103, Penton Publishing Co., Cleveland, Ohio, (1942).

PLASTICIZERS

This class of compounding agents may be defined as high-boiling liquids or, in rare cases, solids, used to toughen and flexibilize a plastic base or to soften it at working temperatures. The effect is considered to be due to a solubilizing action and an accompanying reduction of inter-molecular forces to permit freer movement of the parts relative to one another.

The two fundamental purposes of the plasticizer have been outlined in its definition. They are:

(1) Production of resilient elastic characteristics. By using the correct type and amount of plasticizer, the vinyls produce rubber-like materials, cellulose acetate becomes flexible foil, and the acrylates form resilient coatings.

(2) Development of ease of fabrication. By proper compounding with suitable plasticizers, the thermosetting phenolics flow satisfactorily in the mold, synthetic rubbers are readily "broken down" to a plasticized condition during milling, and polyvinyl chloride is obtained as an extrudable composition. To these two basic purposes a long list of specific reasons might be added. Phosphates, for example, improve the flame-resistance and hydrocarbon plasticizers raise the dielectric strength. The role of plasticizers in thermosetting plastics is limited to providing sufficient flow during molding. During the curing of the resin, it changes from a soluble to an insoluble material. Its relationship to the plasticizer thus changes and plasticizer and resin may no longer remain completely compatible. Excessive amounts of plasticizer may then result in "bleeding out" as the liquid diffuses toward the surface.

The application of plasticizers in the field of thermoplastic resins is, however, broader and more valuable. The wide variety of properties—moldability, tensile strength, impact strength, flexibility, elasticity, and high elongation—associated with thermoplastics is often achieved by the use of the proper plasticizer. The action of different types on a specific base plastic varies according to the solvent effect exerted by the plasticizer. If mutual solubility of resin and plasticizer exists, low tensile strength, high impact resistance and elongation, lower softening point, increased cold flow, and maximum flexibility result. If the plasticizer is of a *non-solvent* type, however, the tensile strength is higher, impact resistance decreases and flexibility is not greatly enhanced. "Bleeding out" also is likely to occur when complete solubility is absent.

When the effect of plasticizers on a plastic base is studied further it is found that the extent of the effect is determined also by the molecular weight of the plastic molecule. Materials of high molecular weight are conveniently compounded with suitable plasticizers to a rubber-like state, whereas the addition of plasticizers to low molecular weight polymers results in excessive softening and cold flow.

SOLVENTS

The addition of a small amount of a solvent to a plastic material results in the formation of a gel structure as the plasticity increases. This is the effect of a plasticizer. As the ratio of solvent to plastic is increased, however, complete liquefaction usually results. The degree of retention of gel-like characteristics on dilution, as evidenced by a continuous nature in the sol and by high viscosity solutions, is directly dependent upon the chemical nature and molecular weight of the plastic. The development and manufacture of solutions and suspensions in plastics engineering is evidenced in the coating and laminating applications of plastics. Each of these will be discussed in subsequent chapters, but the role of the solvents used may be emphasized here.

First, the fundamental rule of solubility, "like dissolves like," applies to the use of solvents with plastics. Each particular type of plastic base may be dissolved in specific solvents for that material. The appropriate solvents have been referred to in the preceding sections which describe the synthetic products. It should be emphasized that the solubility of the thermosetting or heat-modified resins and rubbers refers to the solubility of the uncured material. Decreased solubility due to the cross-linkages introduced by heating prevents solution of the cured product.

Observation of the solubility relationships above illustrates the existence of three main classes of solvents. These are:

Non-polar: typified by the aliphatic and aromatic hydrocarbons.

Polar: including a broad class of oxygenated solvents such as esters, alcohols, ketones, nitroparaffins, and ether-alcohols.

Chlorinated: consisting of both polar and non-polar molecules which contain chlorine as an integral part of their composition. Carbon tetrachloride, chloroform, ethylene dichloride and chlorobenzene are examples.

The most perplexing problems related to the use of solvents arise from the fact that it is often desirable to use a *non-solvent diluent* in

combination with a *true solvent* in order to reduce costs or regulate viscosity; and from the fact that, in some solution applications, a combination of resins must be used, the components of which are not mutually soluble in the same solvent. In solving the first problem, it is not sufficient merely to find the combination of solvent and diluent which will provide a solution of the desired viscosity for a given application. The rates of evaporation of both the solvent and the diluent must be considered. If the solvent evaporates more readily than the diluent, the resin may coagulate without forming a satisfactory film. On the other hand, if a high-boiling solvent is used alone, drying will occur too slowly for practical purposes. Consequently, mixtures of low, medium or high boiling solvents are used with the desired diluent. The final solution must be such that it will "set" immediately after application and must then lose both solvent and diluent at such a rate that coagulation of the resin does not occur and the film dries in a reasonable period of time. It is obvious that the ideal solvent-diluent blend for a particular application can be obtained only after considerable experimentation. Much the same problem exists in solvent applications of many resin combinations. In lacquer formulations, for example, cellulose nitrate must be blended and modified with various gums and natural resins in order to obtain optimum properties. Lack of a mutual solvent in many such instances necessitates regulation of solvent blends which will permit even drying and maintenance of mutual solubility until the film is completely dry. Proper adjustment of the blend, however, insures the production of films which exhibit the desired properties.

COLORING MATERIALS

Two basic types of coloring materials are used in the plastics industry. These are:

- (1) *Colored pigments*, typified by iron oxide, barium sulfate, mercuric oxide, chromium oxide and a variety of other metallic salts.
- (2) *Organic dyes*, which owe their coloring effect to the existence of chromophore groups in the organic molecule.

Of these, the inorganic pigments may be used quite generally in applications in which decreased electrical properties and loss of clearness or transparency are not important. The pigment is often used both as a coloring agent and as a filler. Naturally, however, the fact that a dry, inert powder is being used as a coloring agent

explains immediately the impossibility of producing transparent, glass-like products by this method.

Organic dyes, on the other hand, may be applied in smaller amounts when higher dielectric values and transparency are desired. A variety of conditions including compatibilities, wettability, absence of injurious chemical effect, stability on curing, and dispersability must be satisfied before the dye is acceptable in any resin formulation.

LUBRICANTS

Lubricants, very briefly, are described as materials added to a molding powder formulation to aid removal by elimination of sticking to the mold. Oils, waxes, soaps and higher fatty acids may be used. Typical examples include such materials as stearic acid, metal stearates and montan wax. The lubricant may be added to the plastic mix or may be coated on the interior of the mold before use. The proper selection in each molding composition must be made by the trial and error method. Insufficient lubrication or surface staining are difficulties which must be avoided.

Review Questions

1. What is the importance of each of the following in a compounding formulation:
 - (a) Filler
 - (b) Lubricant
 - (c) Plasticizer.
2. For what properties are each of the following fillers noted:
 - (a) wood flour
 - (b) asbestos
 - (c) mica
 - (d) alpha cellulose.
3. What is the basic difference between the two main classes of plasticizers?
4. List a suitable plasticizer for use with each of the thermoplastic resins.

CHAPTER XXI

MOLDING

The most important fabrication method in the plastics industry at the present time, and the practice which is largely responsible for the rise and development of plastics is molding. Very simply, we may term any method which causes the deformation or shaping of plastics by application of heat and pressure a molding procedure. The subject may be more conveniently outlined by listing the four most important methods of molding, namely,

Compression molding
Transfer molding
Injection molding
Extrusion

These methods all require preliminary or simultaneous application of heat with the pressure. They are grouped, therefore, into the general classification of hot molding methods. A fifth method—cold molding—involves the use of heat only after the molding powder has been shaped by pressure.

The problem of a custom molder is the selection of the most appropriate molding method for each problem. Once the fundamental method has been decided upon, the conditions, which can be varied in each case, must be determined by experimentation. The molding powder used is of primary importance. Different molding procedures are used, depending on whether the resin is thermoplastic or thermosetting. Variations in filler content, type of filler, degree of flow when heated, and curing times are several of the factors which must be considered in adjusting the molding procedure. The second main consideration is the design of the product. Some molded articles are of complex design and thus require a considerable flow period in the mold. The proper molding powder to satisfy this requirement must be chosen and the molding procedure must be adjusted accordingly. Other designed products require metal inserts. The molding method is regulated—particularly the pressures involved—to prevent the shearing off of these inserts as they are held in place in the mold during the initial application of pressure.

Thus, proper control of all of the factors involved in molding is a difficult and variable problem. Each set of conditions and regulations must be determined for each specific case. When the general factors applicable to each molding method are understood, however, the development of proper conditions may proceed without serious delay.

COMPRESSION MOLDING

Compression molding is recognized as the forerunner of all molding methods, for the fundamental idea of shaping a plastic body by heat and pressure was first utilized in compression methods. Baekeland applied compression molding techniques to phenol formaldehyde resins about 1907. Since that time, the use of compression techniques has been marked by continual advance and refinements. The distinctive feature of heating and shaping by pressure of the molding powder *while it is held in the same cavity* has remained unchanged. By other methods—transfer and injection molding—it has been shown that heating and shaping may take place in two separate chambers.

Then, too, the advances in compression molding have not changed the primary purpose for which it was intended. The method is still applied in the majority of cases to thermosetting compounds. Although thermoplastics can be processed by compression molding, the time lost in cooling the molds before removal of the shaped article is a major drawback and thus prevents competition between compression and injection techniques in the thermoplastic field.

Molding Presses.—The equipment used in compression molding may be described for general purposes as consisting of flat plates upon which the mold parts may be fastened and which are capable of being moved toward one another (usually only one moves) as pressure is applied. The plates are supported in position by side-walls or supports. The movable plates, in addition, are held on rams which in turn form part of the hydraulic pressure, mechanical pressure, or air pressure system. Methods of temperature adjustment and control, loading and discharging of the mold cavities, and supplementary pressure units to open the press may form part of the equipment.

The complexity of the apparatus depends directly upon the way in which it can be applied to molding techniques. Thus, hand, semi-automatic, and automatic presses differ from one another in the degree of manual control necessary in their operation. This is the first division of compression molding equipment into specific groups. The next division of molding presses into various groups depends upon their mechanical operation. These sub-divisions include:

Upward Stroke Press: The lower platen is moved on a hydraulic ram, set at the bottom of the machine, toward the fixed upper platen as the press is closed. The die is opened when pressure is released and either the weight of the platen or auxiliary pull-back system separate the die cavity parts. Figure 21.1 shows the principal parts

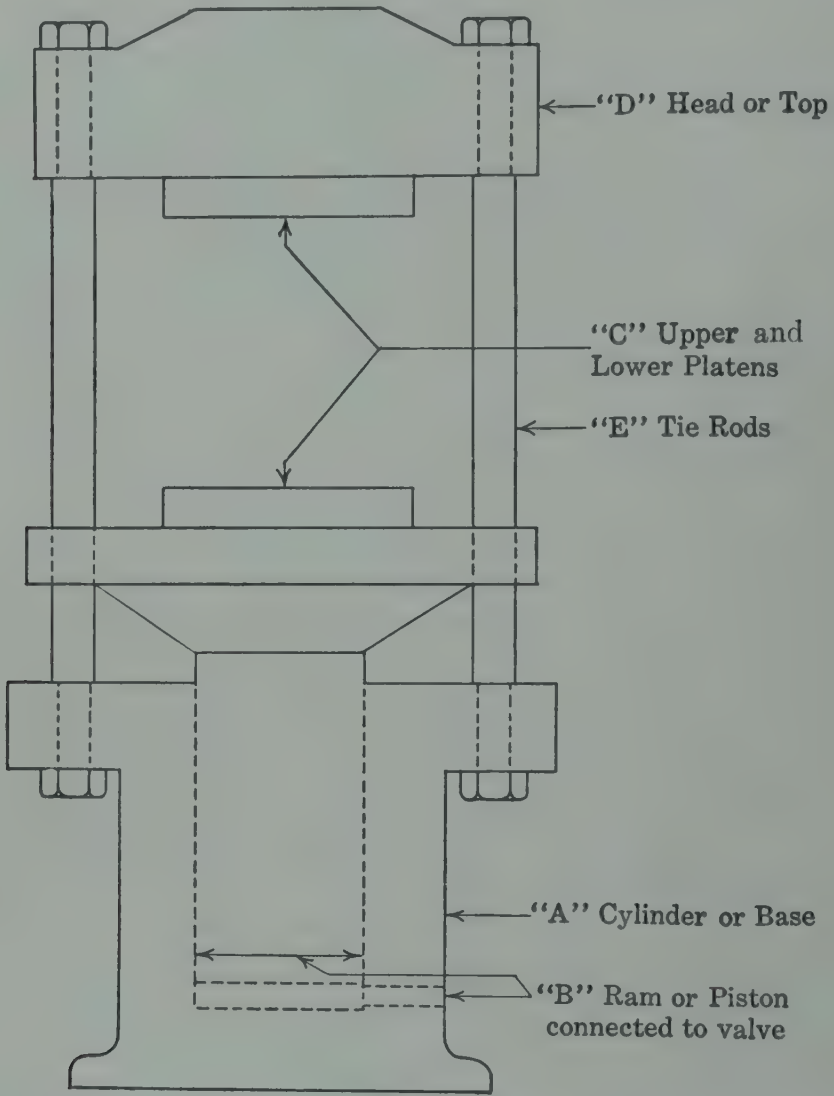


FIG. 21.1. (Courtesy of Technical School of Plastics, Boston, Mass.)

of an upward-stroke press and Figure 21.2 illustrates an actual press in operation.

Down Stroke Press: Otherwise known as an inverted ram type this works on a principle opposite to that above. The upper platen is activated by the ram from above and moves toward the fixed lower

platen. A method of pulling the upper platen back into position must be provided.

Multiplaten Press: A press containing many platens parallel to and separated from one another is particularly adaptable for the forming and curing of flat pieces. Laminated articles are usually cured in this type of press. The pressure is exerted by a single ram which controls all the plates which are free to move. A picture of a multiplaten press is shown on p. 444.

Double Ram Press: The operation of this apparatus is similar to that of the simple up-stroke type, but in order to facilitate the molding of parts containing a deep draw, two rams acting independently and moving toward each other may be used. More rapid production and improved flow in the mold result.

Side Ram Press: One or two side rams which are capable of exerting a pressure at right

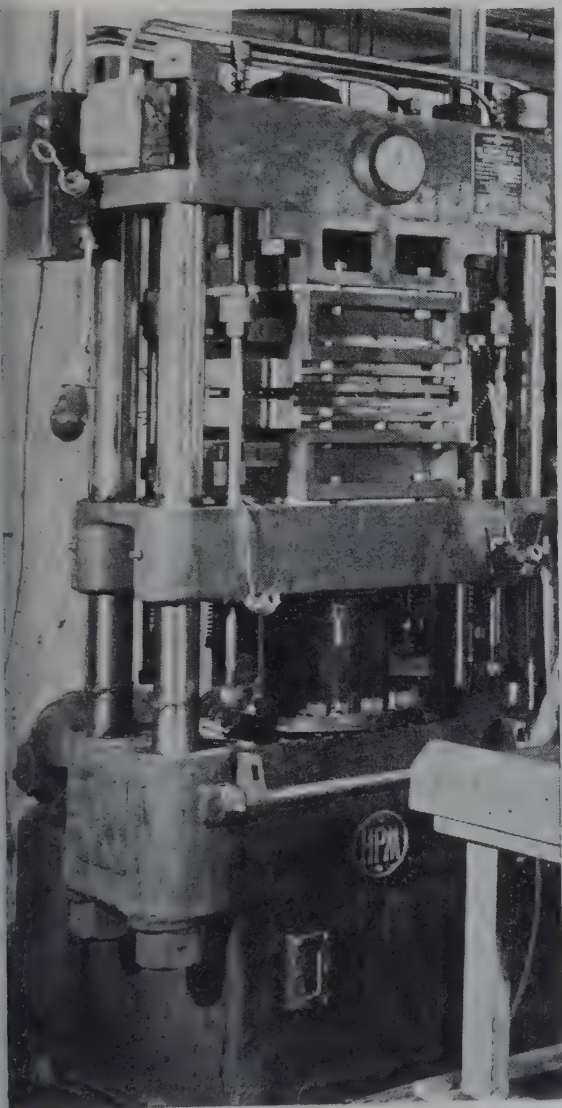


FIG. 21.2. Upward stroke press shown in closed position. (Courtesy of Hydraulic Press Manufacturing Company.)

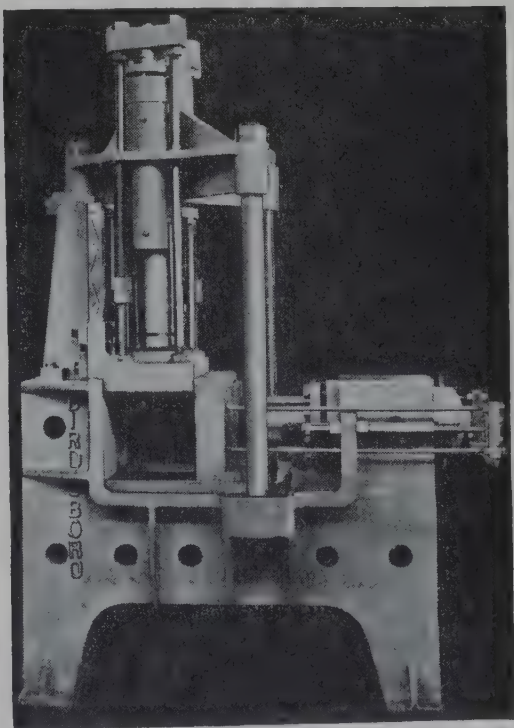


FIG. 21.3. Side ram press. (Courtesy of Birdsboro Steel Foundry and Machine Company.)

angles to the main molding pressure may be used. This type is particularly adaptable when horizontal pressure must be applied on the mold halves during molding, and is represented in Figure 21.3.

Tilting Head Press: The design of this press is used primarily to facilitate the fixing of inserts in the mold cavity or the removal of molded pieces. The upper portion of this press tilts upward at a 90° angle as the press is opened and, as a consequence, the operator is able to reach all parts of the mold cavity for filling, removal, placing of inserts, cleaning, and inspections. (See Figure 21.4.)

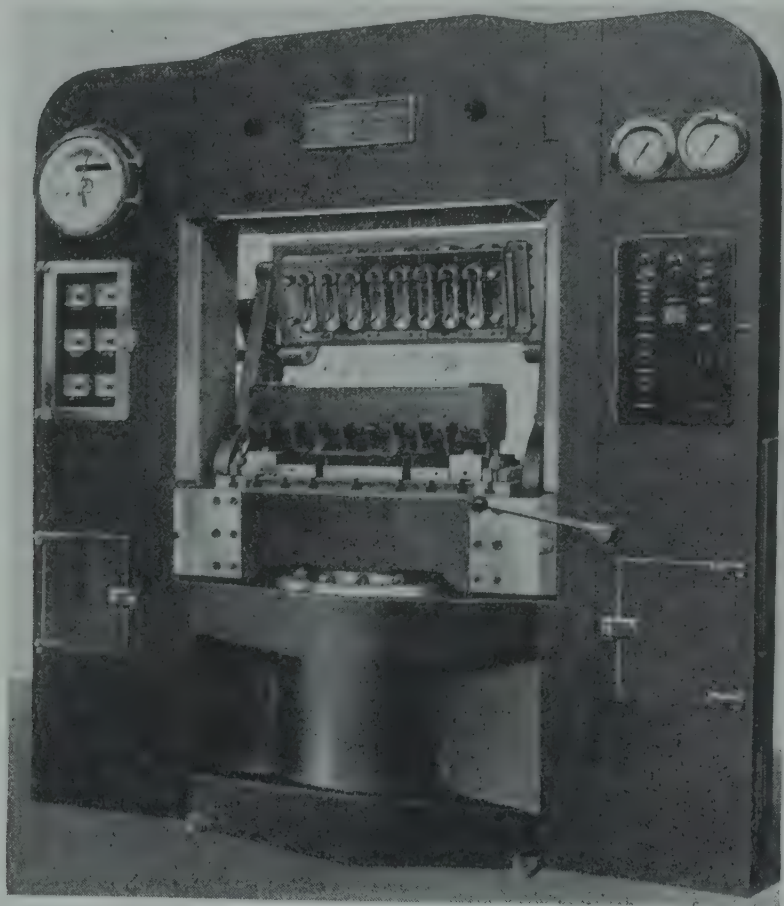


FIG. 21.4. Tilting head press. (Courtesy of The French Oil Mill Machinery Co.)

Rotating Table Press: A special method designed to speed production is that used in the rotating table press. This type involves the use of two sets of dies set on a rotating table. Thus, while one set is being used for molding in the press, the other set may be cleaned and filled with powder. Then when the table is rotated through 180° , the die sets are reversed.

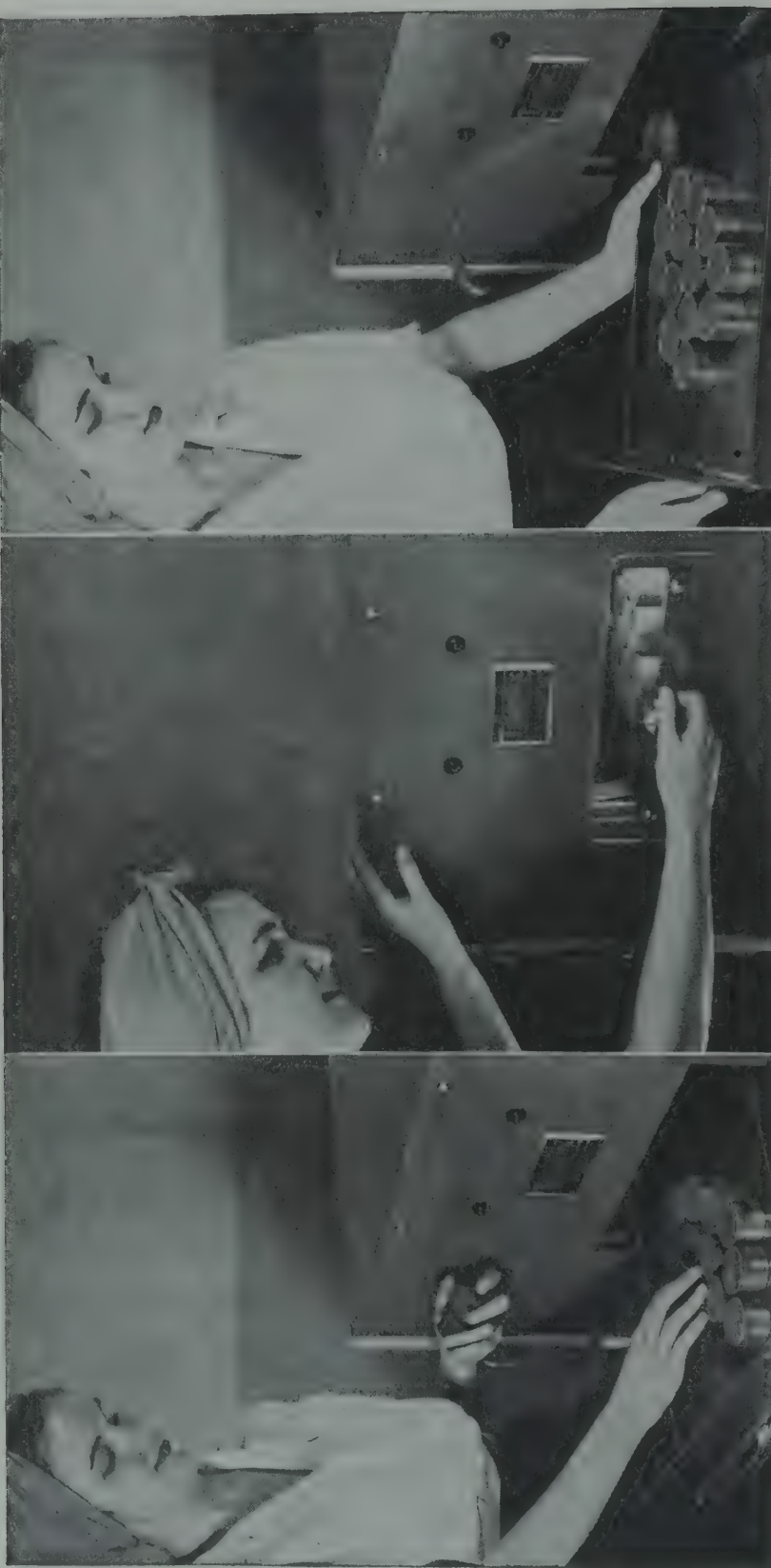
Temperature Control.—Heat is applied to the molding powder by a variety of methods. These include steam heating, super-heated water (supertherm heating), gas heating, electrical and induction currents. The regulation of the temperature of molding is of primary importance. To facilitate this control, many methods of maintaining even, continuous heat over the entire platen surfaces have been tried. As would be expected, those presses which provide most intimate contact of the heating system with the platen surfaces are regulated most readily. Thus, steam heating is popular because platens and mold parts may often be cored for passage of steam and more uniform heating conditions result. Caution must be exercised, however, to prevent weakening of the parts involved.

Temperature readings also should be made as near the surface of the molded piece as possible. Thermostatic methods of control may often be applied when electrical heating is used. A recording temperature controller which supplies a continuous temperature record is recommended for supertherm or steam heating.

Recent advances in pre-heating of the molding powder have facilitated the control of temperatures during molding, for they have eliminated some of the dependence of successful molding techniques upon the temperatures during molding. Electrical, steam, and high-frequency methods have been applied to pre-heating. The latter is incorporated in the technique known as *heatronic molding*.

Heatronic molding is the name applied to the process of pre-heating a plastic by placing it in a high frequency (1–50 megacycles¹) electrostatic field and immediately placing it in a mold where it is cured and shaped under pressure and at the desired temperature. Under the influence of an electrical field, the molecules of a non-conductor, such as a plastic, become oriented so that the positive part of the molecular dipole is nearer the negative electrode and the negative part of the molecular dipole is nearer the positive electrode. When the electrical field is reversed, the molecules rotate. If this reversal occurs two million or more times per second, it is obvious that a tremendous amount of friction occurs among adjacent molecules, with the resultant formation of heat. High-frequency heating differs from all other types of heating in that the heat is generated right in the material being heated, whereas in all other methods, the heat is generated outside and conducted into the material being heated. Consequently, the inner portion of the plastic is hotter than the outer surface (in high-frequency heating) because of conduction from

¹ A frequency of one megacycle means that there are 1,000,000 cycles per second.



A. Drawer is being filled with preforms.

B. Operator simply closes drawer of cabinet. Only when drawer is all the way in does the high frequency current—and red light—turn on.

C. When preforms are heated, adjustable timer turns off current and flashes green light. Preforms are ready to transfer to the molding press.

Fig. 21.5A, B, C. (Courtesy of The Girdler Corporation.)

the surface to the surrounding medium, while the reverse is true when other heating methods are employed. High-frequency heating can be used with thermosetting resins which can then be molded in a compression or a transfer molding press in much the same way that a thermoplastic resin is molded in an injection molding machine. The simplicity of the pre-heating of preforms, from the operator's viewpoint, is shown in Figure 21.5.

The outstanding advantages of heatronic molding are:

1. Rapid, uniform pre-heating of the resin.
2. Marked decrease in curing time, resulting in much shorter cycles.

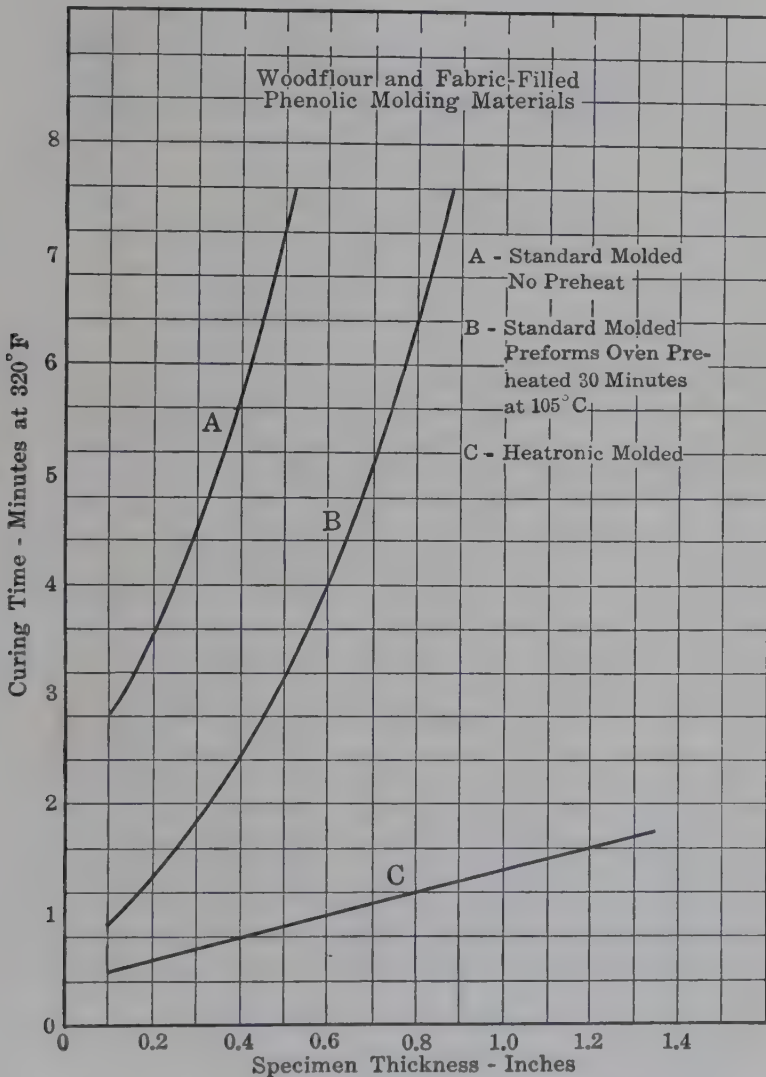


FIG. 21.6. Optimum time of molding specimens of different thickness. (Meharg, *Modern Plastics* 20 (7) 88, 1943.)

3. Satisfactory use of thicker sections than can be used in standard molding procedures.

4. Instantaneous cessation of the application of heat.

The relationship between curing time and thickness of the sample in both standard and heatronic molding procedures is shown in Figure 21.6.

The superior results obtained with heatronic molding of relatively thick sections in a short time are shown in Figure 21.7.

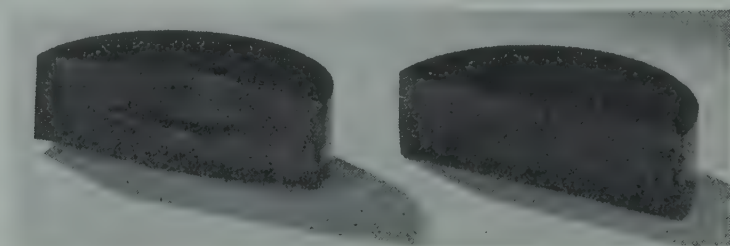


FIG. 21.7. Cross section of disks 3 in. diameter, $\frac{7}{8}$ in. thick molded of general purpose phenolic material at 320° F. Left: Standard molded, 10 minutes cure. Right: Heatronic molded, $1\frac{1}{4}$ minutes cure. (Courtesy of Bakelite Corporation.)

Pressure.—The regulation of pressure is of equal importance with that of temperature. The pressure exerted during molding must be calculated from a knowledge of the cross-sectional area of the molded pieces and, in cases where excessive overflow or “flash” occurs, from the total area of molding material upon which the pressure is exerted. The pressure originates from an oil or water hydraulic system or, in rare cases, from centralized air systems. The hydraulic pressure in most cases depends upon the operation of a centralized pump and accumulator mechanism. The latter affords a means of regulating the pressure which can be supplied to the presses. The presses are connected to the main system by inlet and outlet valves adjusted to supply any pressure desired. Generally a combined low-pressure and high-pressure operation is used in order to supply a low pressure of 300–500 pounds per square inch during closing of the press and higher pressures of 2000–5000 pounds per square inch during molding. The pressure exerted may be calculated from the following equations:

$$RP = LP \times RA$$

$$MP = \frac{RP}{MA}$$

where

RP = ram pressure on press

LP = line pressure of main system

RA = ram area (sq. in.)

MP = molding pressure in lbs. per sq. in.

MA = projected area of the molded piece

If greater accuracy is desired, the dead weight of the platen, ram and mold must be subtracted, in the case of an upward stroke press, from the ram pressure, i.e.

$$MP = \frac{RP - DW}{MA}$$

Pressure may also be applied in a mechanical press by means of a crank screw or toggle device.

Molding Operation.—The following steps are included in the technique of compression molding:

Filling or Loading of Mold: The loading methods are variable. The powder may be charged into the mold by volume or weight measurement by means of a simple manual hopper feed, or by automatic methods. Inserts must be positioned in the mold cavity (Figure 21.8A) and split parts must be assembled before charging. Most rapid handling of the molding powder results from preliminary tabletting or shaping of the dry powder. This latter operation is known as preforming. When it is desirable to reduce the bulk of the powder as compared to that of the molded piece (i.e., bulk ratio) or to facilitate measuring or flow of the molding powder, preforming is desirable. Described in general terms, preforming consists merely of compressing dry powder into pills, tablets, or forms approximating the shape of the final piece. Charging into the mold is carried out with maximum cleanliness by placing in each mold cavity the requisite number of tablets (Figure 21.8B).

Closing of Molds: The halves of the mold are closed slowly with low pressures to prevent escape of the powder, to permit the escape of accumulated gases and to allow the heat to thoroughly penetrate the molding powder. Also, if high pressures and rapid closing were applied, the danger of shearing off insert pins would be great. When preheating is applied, however, the mold may be closed more rapidly for these dangers are decreased.

Breathing: After preliminary closing of the mold it is often advisable to "breathe" or "gas" the molding assembly to permit the escape of gases trapped or produced by curing reactions within the

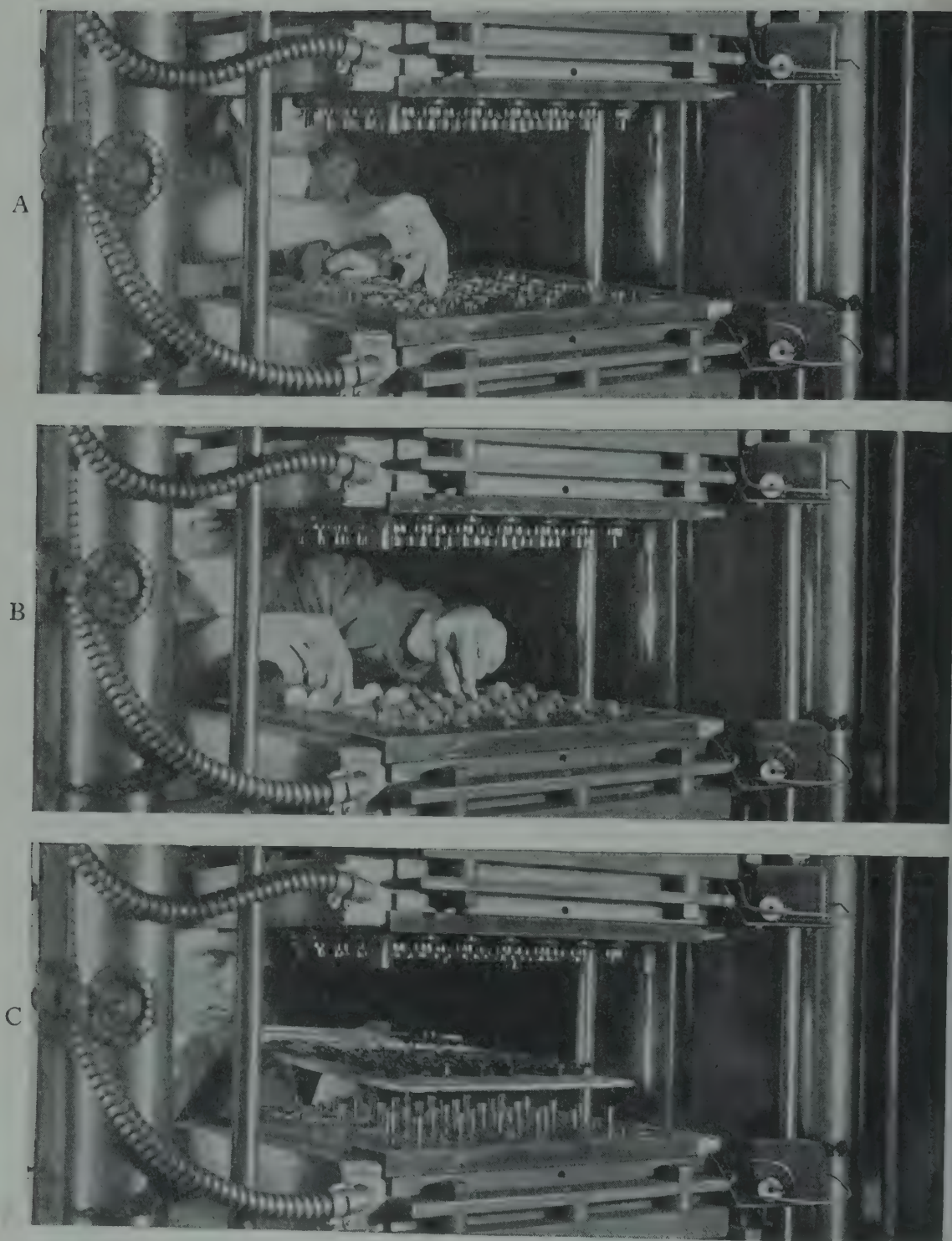


FIG. 21.8A, B, C. Steps in a typical compression molding cycle. A—Positioning of inserts. B—Filling of mold. C—Removal of molded product.

mold. Thus, when the mold parts are momentarily separated, the gas escapes and the danger of getting porous or blistered pieces is minimized.

Curing: The time allotted in the mold to the hardening of thermosetting resins is known as the curing time. As the resin passes into the final stages of reaction, the desirable physical and chemical properties are realized. Much variation in curing times is encountered because of differences in resin types, production control of the resins, amounts of hardening and catalyzing agents present, thickness of molded piece, temperature, and ultimate properties desired. Time and temperature control are particularly important, for with under-cure, porous surfaces, blisters, and poor dimensional stability result. With over-cure, brittleness, increased costs, and poor colorability result.

Ejection: The simplest method of removing pieces from the mold is by a manual operation. Since the time involved in this is often objectionable, automatic means are provided. Knockout or ejector bars and pins which are built into the mold, and operate automatically as the mold opens, force the piece from the cavity. The operator may then simply rake or collect the released pieces (Figure 21.8C). Threaded parts may be removed by a power chuck. It should be remembered that in cases where thermoplastic parts are being compression molded, cooling of the molds must precede ejection. Even in cases of thermosetting parts, cooling by artificial means is often carried out in order to prevent distortion of the object when it is ejected.

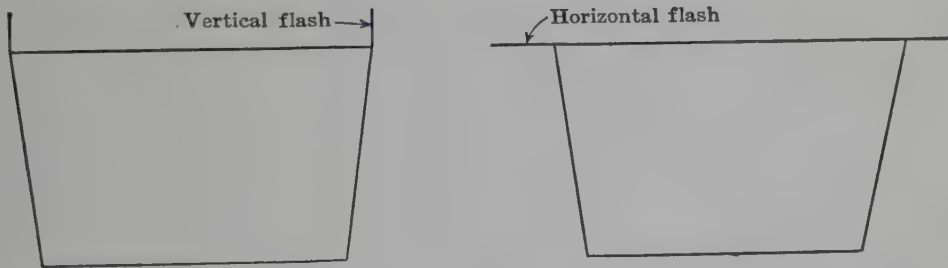


FIG. 21.9

The final operations in the production of a molded piece by this method are concerned with machining operations. The flash, i.e., the fin formed by the plunger as the overflow molding material is caught and pressed (see Figure 21.9), must be machined off before supplementary buffing, drilling, sawing or lathing operations are carried out.

Typical products obtained by the operations illustrated in Figure 21.8A, B, C are represented in Figure 21.10.

TRANSFER MOLDING

The application of injection molding methods to compression molding press and materials is involved in transfer molding. Although pressure and temperature may be controlled as already described, heating of the molding material is carried out in a separate chamber preparatory to forcing the softened material by the application of pressure into the desired form. The mold dies consist, thus, of two chambers. The first, the *loading well*, may be filled with the molding powder. As the plunger moves into the loading well, pressure is exerted, a softened condition is reached and the plastic is forced through a narrow opening into the mold cavity where final curing takes place. The cured product is then broken off at the gate and the loading well recharged. The gate and the slight amount of well residue are machined off and discarded, for the material, being thermosetting, cannot be reused. This process is illustrated in Figure 21.11.

This method of molding is particularly applicable for the molding of pieces containing complex inserts, complex structures, and intricate designs. Powders having a high bulk ratio may be molded with less difficulty of thick flash and variable density. The softened condition of the molding material as it is pressed into the final form is responsible for these benefits.

INJECTION MOLDING

The popular method of molding thermoplastics by injection molding was introduced about 1931 in this country and started its rapid progress in the industry about 1935. The principle involved in this process is similar to that of transfer molding. Heating of the molding material in a separate chamber precedes the actual shaping of the product. Injection molding may be summarized, therefore, as a process of loading, heating, injection into the mold, cooling and ejection.

Injection Molding Equipment.—The majority of injection molding machines operate automatically at all steps from the initial loading to the final ejection. Automatic controls for the regulation of temperature, pressure, and molding cycles are a fundamental part of the equipment. In but few instances does the operation depend in part upon manual processes. In a typical press, the plastic is

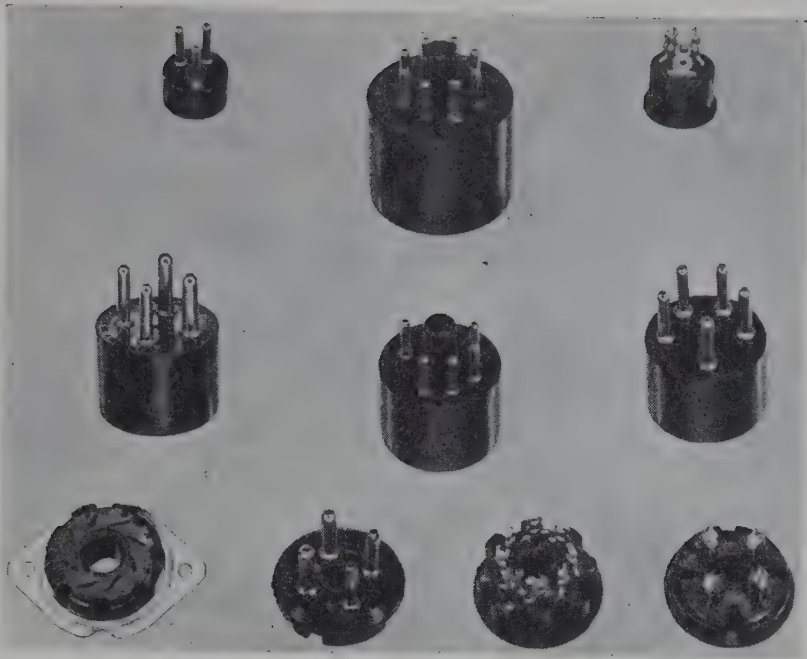


FIG. 21.10. Typical objects made by compression molding. (Courtesy of Hydraulic Press Manufacturing Company.)

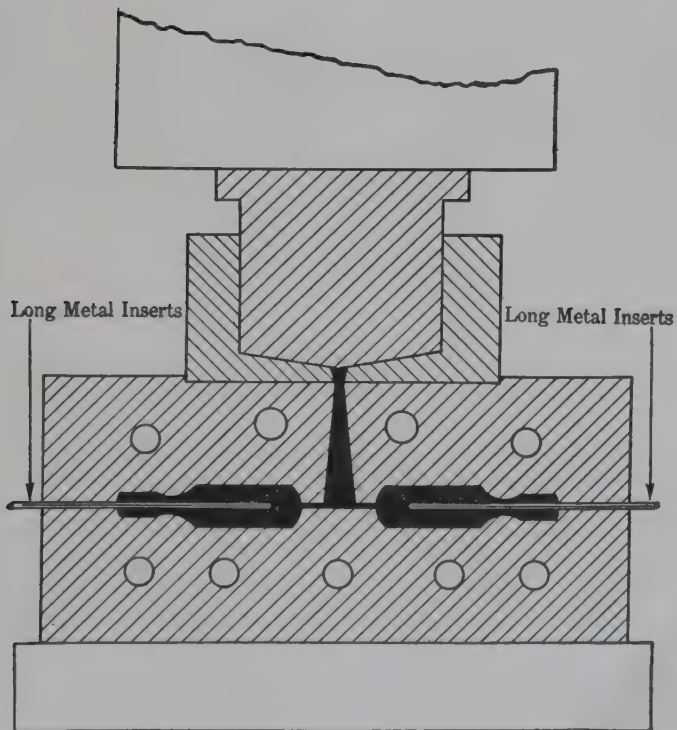


FIG. 21.11. Transfer molding. (Courtesy of Bakelite Corporation.)

introduced through a hopper which is connected to a screw arrangement by means of which the flow of the molding powder into the heating chamber may be controlled. This rate of flow is synchronized with the movement of a piston at the extreme end of the heating chamber. The movement of this piston is accomplished by either mechanical or hydraulic arrangements. In the former, the piston is actuated by gears and spring housing; in the latter case, hydraulic pressure similar to that described in connection with compression molding is applied. As the piston moves forward in its injection stroke, it forces the heat plasticized molding powder in front of it and through the chamber into the mold cavity.

Softening of the thermoplastic in the heating chamber depends on intimate contact of the molding material with the heated walls of the chamber. To facilitate continuous movement of the powder through the chamber and even heating, a *spreader* is placed in the chamber. This torpedo- or pineapple-shaped core evens the flow of plastic, prevents localized overheating, provides complete softening, and by streamlining the flow, prevents partial entrapment of the plastic.

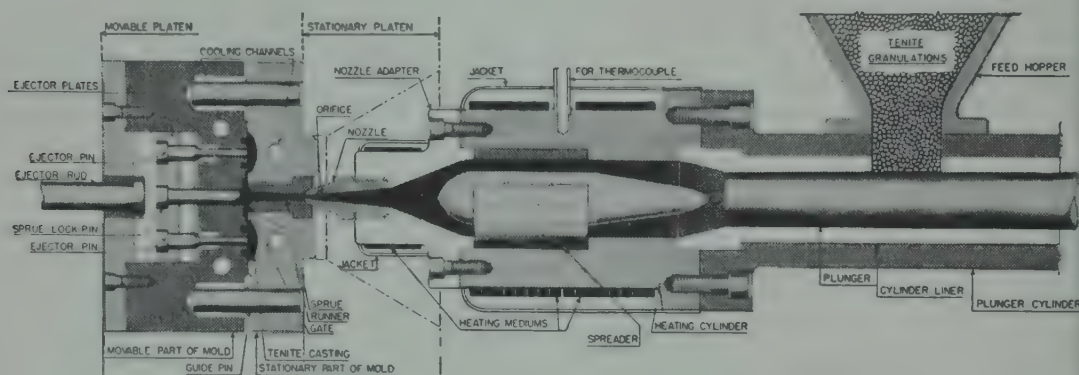


FIG. 21.12. Sectional view illustrating general method of injection molding.
(Courtesy of Tennessee Eastman Corporation.)

The half of the mold through which the plastic is introduced is usually stationary. The other half moves into position along a horizontal plane. See Figure 21.12. The two sections are held firmly closed by pressure arising from an independent source and are released when cooling of the molded form has proceeded to a stage sufficient for hardening. Ejection by knockout bars and pins as with compression molding may then take place.

Special Processes require the application of multiple-injection machines. When pieces are formed by plastic material being injected

from more than one source they are said to be multiple-injection molded. Caution must be exercised in such a case to prevent the formation of *weld lines*. These are lines of weakness resulting from insufficient inter-flow of plastic from two sources as they meet in the mold.

Temperature.—Heating methods are similar to those of compression molding. Steam and electricity are used most frequently. The temperature of the heating chamber, and, particularly, the orifice, must be controlled so as to permit desirable flow without decomposition of the plastic. Also, the temperature of the mold must be controlled, frequently within narrow limits, and the rate of cooling must be carefully regulated. If too rapid cooling occurs, internal stresses are set up by the uneven hardening, but if the cooling takes place too slowly, the cost benefits of injection molding will be lost. Then, too, special effects, such as the molecular orientation in polyvinylidene chloride (p. 308) may be altered by the mold temperature applied and the rate of cooling.

Molding Procedure.—The general procedure applicable to injection molding has been summarized above. Since the operation is largely automatic, the control of the process is dependent upon the conditions of loading, heating, injection, and hardening which must be determined by trial and error for each individual case. The variable factors include:

1. *Materials feed:* Since this is usually synchronized with piston action, its operation is not independent.

2. *Piston stroke:* The variables involved in the stroke of the piston include time cycle and amount of material injected at each stroke. The usual amount of a "shot" is 2–6 ounces and as many as 6 cycles may be completed in a minute, but this variable is largely dependent upon the size of the piece and the softening characteristics of the molding powder. Some multiple-injection machines feed 16 ounces at one time while weights as high as 36 ounces have been claimed. Pressures as high as 30,000 pounds per square inch on the plunger surface may be built up to force the plastic forward. This variable in turn determines the time of the molding cycle for it alters the speed with which the mold cavity may be filled.

3. *Heating cycle:* The temperature and time are variable factors in the control of heating chamber conditions. The degree of flow desired may be adjusted by regulation of these factors.

4. *Orifice size:* The flow of the softened plastic will be dependent upon both the size and shape of the orifice connecting the heating chamber to the mold cavity.

5. *Mold design:* The structural complexity and area of the designed mold cavity will have its effect upon molding conditions—temperature and pressure. The number of units which can be molded at one stroke of the piston depends upon the weight and shape of each unit. A resultant effect on rate of production and cost figures is involved.

6. *Mold temperatures:* As already indicated, rates of cooling determine the amount of internal stress and superiority of the surface finish.

7. *Mold clamping pressure:* The separate mold halves are held in a clamped position during molding. For true duplication of design and placement of inserts, the clamping pressure must be capable of withstanding the pressure set up by the plastic material as it fills the mold.

The design of the mold cavity used in injection molding and the terms used in naming its parts are discussed in Chapter XXII.

A variation of the injection method known as *jet molding* has been successfully applied to both thermoplastic and thermosetting resins. The details are similar to those previously described in most respects, but in this case excessive heat is provided only at the nozzle while moderate heat is provided in the preheating chamber. Then, during opening of the mold, cold water may be circulated to cool the nozzle

to recommended temperatures in order to prevent premature hardening of thermosetting types. It is often referred to, as a consequence, as the hot-cold-nozzle process. The thermosetting types are applicable, because the high heat necessary to soften the plastic is applied only momentarily. A favorable, constant hardening temperature is maintained in the mold and rapid curing occurs because the resin has been raised to the optimum temperature for curing before injection into the mold.

EXTRUSION

When a plastic is softened and forced through a nozzle which forms the desired shape, the operation is known as extrusion. The mechanics

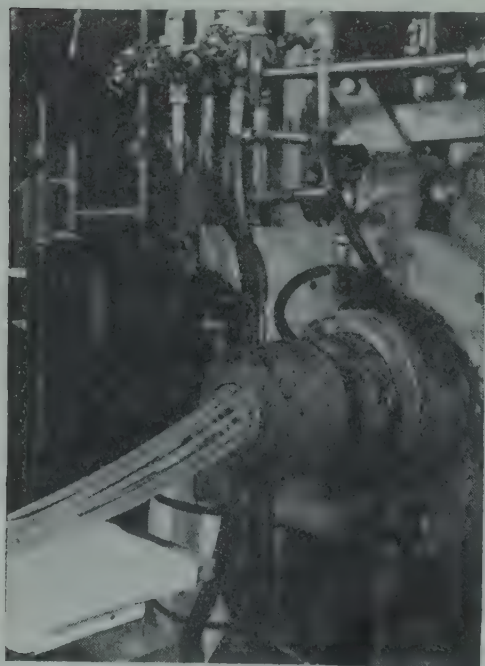


FIG. 21.13 Extrusion of cellulose nitrate rods. (Courtesy of Nixon Nitration Works.)

of the process are very similar to those of injection molding. The continual feed through the die nozzle is maintained by means of a worm-screw. This provides a continuous pressure of plastic at the orifice. The feed is, therefore, continuous rather than intermittent as in injection molding (Figure 21.13). Although provided with a heating chamber which plasticizes the material to the proper stage, the extrusion equipment is often run jointly with a rubber mill. The raw material can be pre-softened on the mill and fed to the extrusion apparatus as desired.

Review Questions

1. What are the fundamental differences in the techniques of (a) compression molding and injection molding, (b) transfer molding and injection molding?
2. Outline the compression molding process by steps.
3. What is "heatronic molding"?
4. Outline the injection molding process by steps.
5. Describe the extrusion process.

CHAPTER XXII

DESIGN OF MOLDS

It is a long step from the preliminary artist's sketch of a plastic product to the production of this article in commercial quantities. The picture created by the artist's pen goes through a well-ordered series of steps intended to organize and adapt the article to the art of plastics manufacture. The design of the molded piece must be suited to certain requisites of the molding operations, but it must, on the other hand, satisfy the requirements associated with its ultimate service. Mechanical strength, electrical and heat resistance, and chemical behavior must be adequate. Likewise, flow in the mold, shrinkage, ejection from the mold, curing times and bulk factors are typical of problems important to the processing.

The artist's sketch must, therefore, be interpreted into mechanical requirements and necessities by the draftsman and the engineer. In collaboration with the artist, the product may be designed to satisfy both aesthetic and performance requirements. The model may then be constructed from the drawing prior to mold design and construction.

DESIGN OF MOLDED PIECE

Various fundamental factors important to the design of a molded piece may be listed. These include:

Wall Thickness.—The design should involve sufficient wall thickness in all constructed parts to satisfy mechanical, electrical, heat or chemical requirements, but it should be remembered that the molding methods also involve certain limitations. In compression molding, curing of thick walls takes place at too slow a rate; in injection molding, thin walls set, during cooling, so rapidly that the mold is incompletely filled. Uniform cross-sections are recommended in order to maintain even curing or cooling and to prevent strains which might result from uneven shrinkage. Allowance must be made for the weakening effect of cuts, holes, and slots in calculating thickness. Reinforcement by struts or ribs may often be employed. Sharp corners should be avoided, and radii corners or fillets should be used instead, as illustrated in Figure 22.1.

Inserts.—Simple assemblies employing inserts, i.e., parts made of such materials as metal, paper, or premolded plastic which are useful as functional members during service, may be molded with little difficulty. Use of such methods often avoids more complicated designs. In compression molding, the pressure is applied while the molding material is in the solid form. As a consequence, high pressures are created in the cavity of the mold as the mold is closed. In transfer or injection molding, the pre-plasticization by heat softens the molding material and prevents excessive localized pressure during molding. As expected, the two latter methods are most adaptable to the use of inserts. Inserts are often used, however, in compression molded pieces. This process is most adaptable to inserts parallel to the direction of closing. Those placed perpendicular to this direction may be sheared off during closing. This is particularly true if the insert or pin is excessively long or slender.

Anchorage of the insert in the molded piece depends upon the type being used. Metal inserts are generally used and in such a case the shrinkage of the plastic, since it is greater than that of the metal, causes the insert to be thoroughly gripped. The effect is aided by knurling designs or undercuts on the metal. (See Figure 22.1.) The anchorage is so good that in some cases the insert may be positioned after the piece is molded by forcing the insert into cavities provided for the purpose immediately after ejection, and before the plastic has cooled. In other cases, the insert is positioned

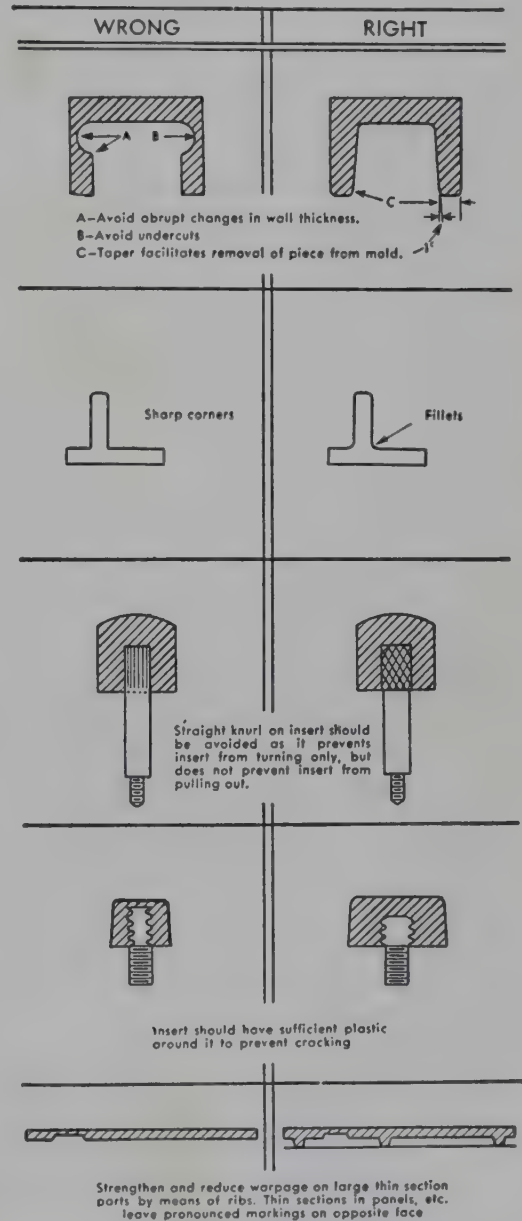


FIG. 22.1. (Petho, *Modern Plastics* 20, (4) 77, 1942.)

on pins in the mold and removed from them after the piece has been formed.

Threads.—Threads may be produced readily in a molded piece. The product should be designed in such a way as to facilitate removal. The threaded piece may be unscrewed by hand or with a power chuck; or it may be formed in a split mold. The threads, as with inserts, should be positioned so that the main plastic structure perpendicular to the thread does not end within $1/32''$ of the thread.

Tolerances.—The tolerance (i.e. dimensional variation permitted) should be regulated in design specifications to values commensurate with economical molding and suitable performance. Excessively small tolerances prohibit rapid production with a minimum number of rejected pieces. The values which may be termed "excessively small" depend upon the molding method used, type of mold, axis direction relative to the direction of closure, shrinkage of parts, and the type of molding powder being used. The general values of $\pm .002$ inch per inch in the direction perpendicular to pressure direction and $\pm .005$ inch per inch in the direction parallel to the pressure direction can be reached if necessary, but values of $\pm .005$ inch and $\pm .008$ inch respectively are more readily obtained. Difficulties are often eliminated by redesign to avoid dependence of great accuracy upon plastic parts.

Shrinkage.—Any calculations of tolerance values and mold measurements necessarily involve comparisons of the shrinkage of the plastic and metal as the temperature is varied from molding temperature to room temperature. The correction factors may, however, be determined by comparison of the expansion coefficients of plastic and metal. This correction value may then be used in designing the mold to the correct dimensions. Complex structures and varying cross-sections are avoided to eliminate strains due to uneven shrinkage.

Undercuts.—This term describes any part of the molded piece which prevents direct removal from the mold. The expansion of transfer and injection molding has greatly extended the possibilities of molding plastic articles containing undercuts. Solution of the problem of preparing such a mold may involve (a) split molds or movable parts held in place by side rams or mold chase (see p. 427), (b) machining, (c) use of internal cores which can be dissolved or melted out after molding, and (d) assembly of parts after individual moldings.

The most important of these methods is that involving the use of split molds. This process is illustrated in Figure 22.2, which

shows a cross section of the mold used for making a spool. The two halves of the split cavity, *A* and *B*, are held firmly together by the mold chase, *C*, and the lower part of the core, *E*, serves as the bottom plate. The molding powder is forced by the top plate or plunger, *F*, into the space between the core pin, *D*, and the split cavity parts. When the curing is complete, the split cavity parts, together with the spool, are ejected from the chase by means of the knockout pins. The two halves of the split cavity are then separated leaving the molded spool.

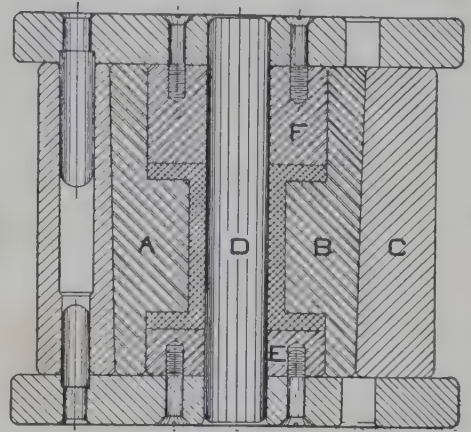


FIG. 22.2. Spool mold (split cavity). (Courtesy of Bakelite Corporation.)

Draft or Taper.—A slight draft or tapering of the molded piece is necessary for proper molding of the plastic. Ejection from the mold is facilitated by proper draft of the contacting sides. The degree of tapering recommended depends upon the type of mold, the procedure being applied and the dimensions of the piece. (See Figure 22.1.)

Flash Marks.—When the mold is closed and pressure applied to the molding material, some of the excess is forced out between the moving parts of the mold. After ejection, this flash is machined off and the marks remaining from this operation are known as flash marks or parting lines. In the design of any plastic article these should be placed at inconspicuous locations. Their appearance on smooth, rounded surfaces and orderly patterns must be avoided. The thickness of the flash line depends upon the perfectness of fit between mold parts and upon the pressures maintained. The fins are generally smaller in transfer and injection molding than in compression molding.

Miscellaneous Effects.—A variety of special effects may be incorporated into the design of a plastic piece. The use of ribs to strengthen thin sections is shown in Figure 22.1. Holes may be formed by molding around core pins. Metal inlays are sometimes used in order to produce desirable surface effects. In one process, a metal inlay may be obtained by first molding the piece with a suitable cavity which is 0.020 inch deep. A small piece of brass is fitted into the bottom of this cavity. The top metal, usually chrome brass, which is provided with a burled edge or skirt, is then forced into the cavity under pressure and becomes permanently locked in

CROSS SECTIONS OF INLAYING PROCESS

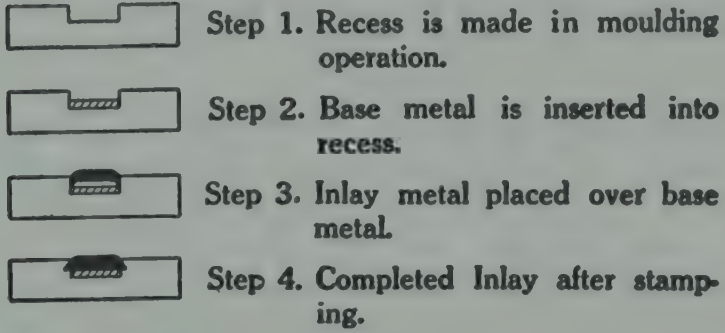


FIG. 22.3. (Courtesy of Plastic Inlays, Inc.)

the plastic. No heat is necessary when a thermoplastic resin is used, but heat is used with thermosetting resins, being conducted through the top metal to the plastic. Figure 22.3 illustrates one process of making metal inlays and Figure 22.4 illustrates some commercial applications of metal inlays.

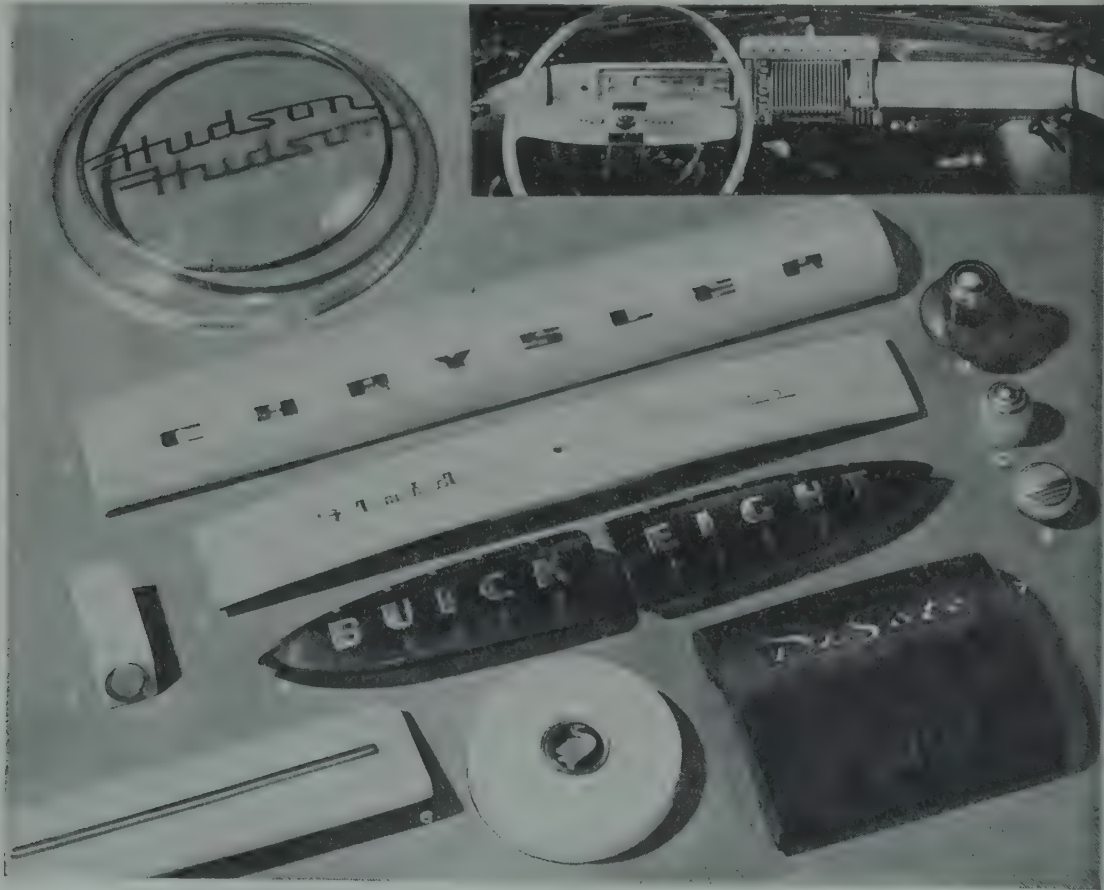


FIG. 22.4. Ornamental metal inlay in plastic. (Courtesy of Plastic Inlays, Inc.)

MOLD MANUFACTURE

When the design and characteristics of the molding have been established, the next step is that of constructing a suitable mold. The manufacture of the molds according to the specifications provided is concerned with metals and their working. Consequently, little time is devoted to the problem here. The most popular metal is steel which may be flash hard chromium plated if desired in order to provide longer wear and superior surface finish in many cases. The two basic types of steel which are most frequently used are tool steel and machine steel. The former is harder and, therefore, subject to less distortion under prolonged treatment with heat and pressure. Such long-life characteristics are often offset, however, by the machining and hobbing difficulties involved in their formation. With machine steel the opposite is true. Ease of machining and hobbing is offset by the softness and poor wearing qualities.

The heat-treatment of the steel molds is regulated to produce as favorable a combination of properties as possible. Treatment will depend upon the type of steel used. Greater difficulties are encountered with machine steel, for the hardening process is more lengthy and productive of a hard shell over a soft core. Cracking or crazing may then occur.

The two most common methods of forming the mold are machining and hobbing. Machining consists simply of cutting the mold cavity in the shape of the desired piece. Hobbing involves the use of a relatively soft steel and a hardened steel hob. By forcing the hob into the softer metal, the mold is formed. This operation is illustrated in Figure 22.5. A depression which is the negative of the desired form results by displacement during hobbing. Faithful reproductions of all features machined into the hob are reproduced in the blank as shown in Figure 22.6. Hobbing may be done in several stages if the desired form is large. Final assembly of the blank is preceded by hardening and polishing.

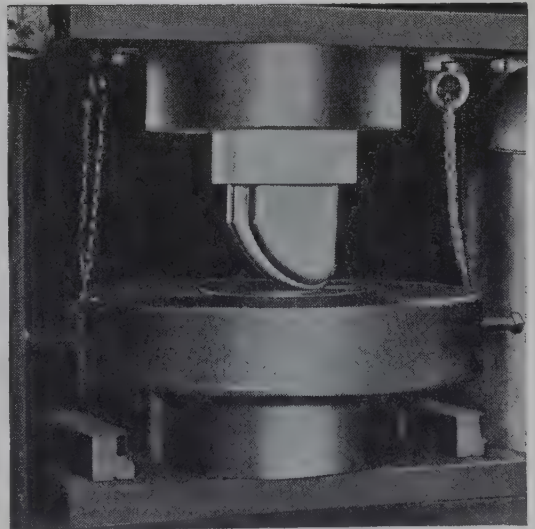


FIG. 22.5. Forming a mold by hobbing. (Courtesy of General Electric Company.)

Other metals may be applied to mold manufacture. Injection molds, for example, may be formed of softer materials at the cavities because maximum pressure is not applied at these points. Beryllium-copper alloys, zinc alloys and brass have been used in small amounts.

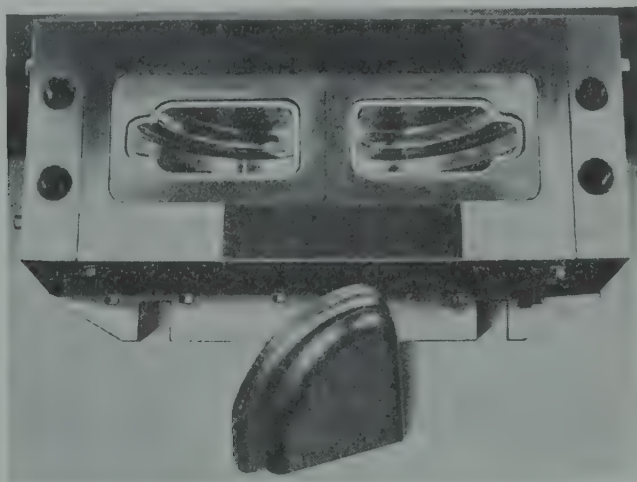


FIG. 22.6. Mold produced by hobbing and hob used.
(Courtesy of General Electric Company.)

DESIGN OF MOLD

The first subdivision of molds must be into the three main classes of compression, injection and transfer molds, corresponding to the methods of molding. Subdivision from this point may be based upon the operation of the mold. Although injection and transfer molds are almost universally designed for semi-automatic or automatic operation, the molds used in compression molding vary from the simplest hand-operated types to semi-automatic and finally to automatic. In the latter cases, the molds are assembled in the press, and loading and ejection are mechanically controlled according to the refinements of the mold being used. Since the greatest variation occurs in compression molds these are discussed at length.

Compression Molds.—The best method of classifying compression molds is based upon the design and working of the mold itself. Three basic types: positive, semi-positive and flash molds are known.

1. *Positive.* The positive mold is illustrated in Figure 22.7. In this type, the *top force* or plunger telescopes into the mold cavity which is contained within the confines of the *chase*. The pressure is resisted from below by the *lower force*.

Many modifications of this fundamental structure may be applied. For example, to decrease the frictional forces involved by telescoping

parts, the top force or plunger may be of a smaller diameter than the cavity in which it is moving. This may be true for the entire length with the exception of the bottom $1/8''$ or $3/16''$, where the true

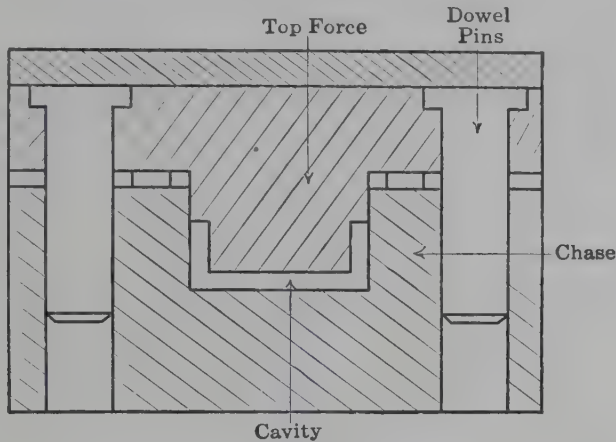


FIG. 22.7. Positive mold.

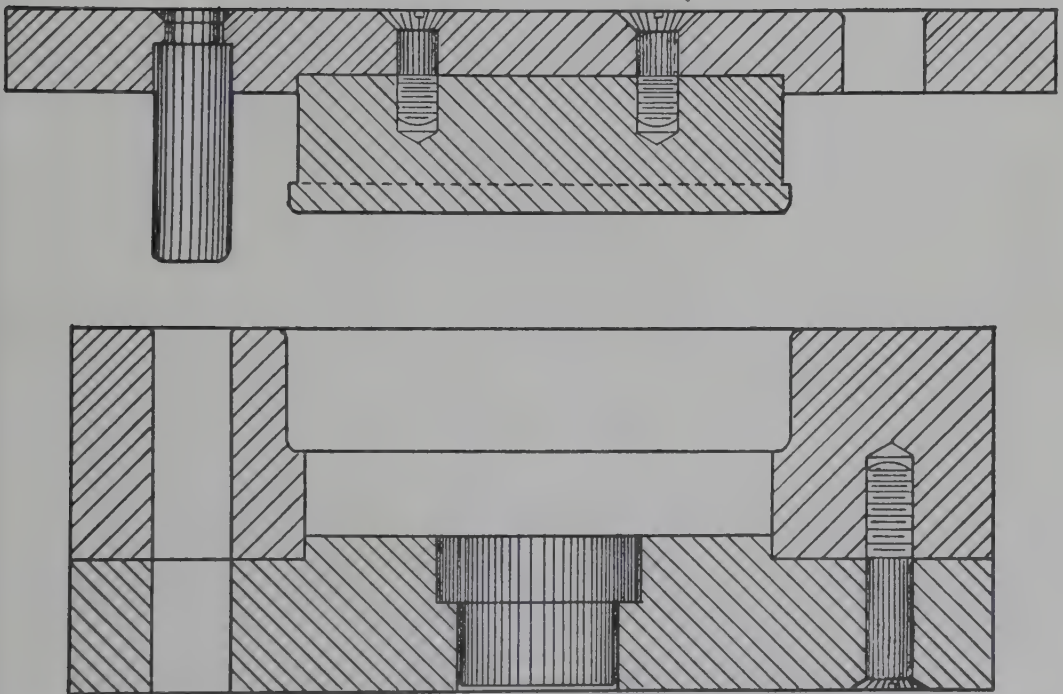


FIG. 22.8. Landed positive mold. (Courtesy of Bakelite Corporation.)

diameter is required for application of pressure on the piece being molded. An alternative is the provision of a shoulder in the mold cavity. The plunger telescopes onto this landed area. This type is typical of a "landed positive mold," and is illustrated in Figure 22.8.

The fins or *flash* produced in the positive mold are vertical and generally very thin because of the close fit of the telescoping parts. Although this mold is difficult to use when close vertical tolerances are necessary, because the distance the plunger travels is dependent

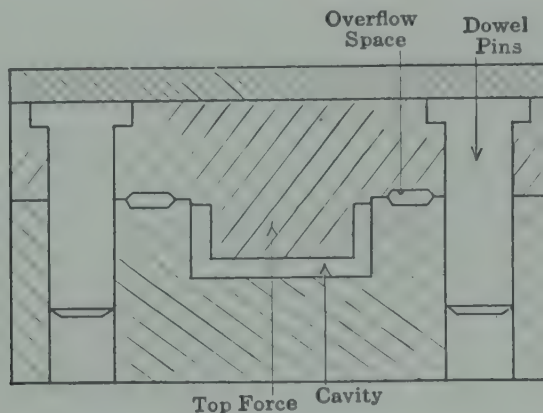


FIG. 22.9. Semi-positive mold.

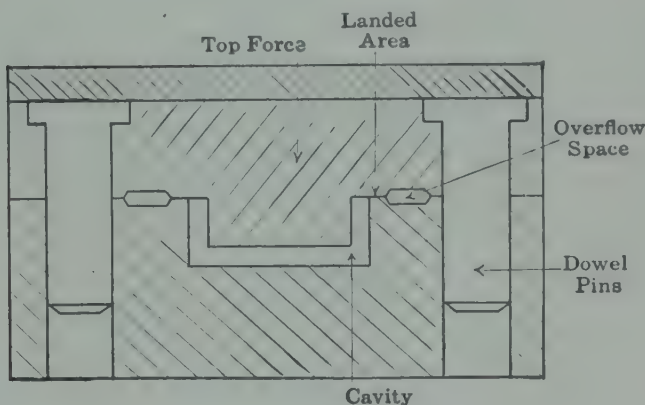


FIG. 22.10. Flash mold.

upon the mold charge, powders of high bulk ratio are easily handled because a deep cavity can be conveniently machined for their use.

2. *Semi-Positive*. In the operation of this mold, the telescoping of the top force occurs only during the last $1/32''$ to $1/8''$ of the mold closing. This is illustrated in Figure 22.9. The positive pressure on the molded piece exists, therefore, only at the final stages of closing. The flash in this case is vertical at the telescoping surfaces and, if excessive, a horizontal flash on the landed areas may be formed.

3. *Flash or Overflow*. In this designed form the mold may be distinctly divided into upper (or plunger) and lower (or cavity) halves. It is illustrated in Figure 22.10. The absence of telescoping parts causes the formation of flash along the landed or cut-off areas

over which the upper and lower parts come in contact. The thickness of the flash is regulated by control of the pressure and variation of the cutoff area. By designing depressions on the landed area, a cavity for excess overflow is provided and the pressure is confined to a small area. The thin flash which results can be easily machined. Back pressure to control dimensions is provided by use of a small excess of molding material. Too large an excess must be avoided in order to prevent the formation of a thick flash which could be machined only with difficulty. The difficulties of flash molding are those of machining excessive flash and the production of less compact products than those obtained by positive or semi-positive types. Also, difficulty is often experienced with molding powders of high bulk ratio because there are definite limitations to the depth of the cavity which can be used in each specific case.

These three types of compression molds summarize the major possibilities, but broad variations for specific purposes may be designed and applied. Thus, split molds are used when undercuts make them advisable; flash filler plate molds are designed to accommodate bulky powders; complicated ejection methods are added to facilitate removal. Fundamentally the parts of a compression mold may be summarized as follows:

Pressure plates: These provide a means of transmitting pressure to the molding charge. They are often fitted with steam or electrical heating devices. In multiple cavity molds, built up from many individual molds, the pressure is transmitted by the pressure plates to *force plugs* or *bottom plugs*. These may be considered as pistons.

Chase: This is the fundamental part of the mold which encloses the mold cavity. The cavity may be machined into this enclosure or in the case of multiple cavity molds the chase may be used to retain the individual cavities.

Cavity: This is the open space in the chase where actual shaping of the plastic part will occur. The individual cavities of a multiple cavity mold are referred to as dies.

Ejector bars and pins: The ejection of the molded piece from the mold is accomplished by knockout pins supported on the ejector bar. The pins usually contact the piece at its base and, as the lower plate moves downward, the piece is forced out.

In many principles, the construction of molds for other types of molding is similar to that of compression molds.

Injection Molds.—In the design of injection molds space in the mold must be provided for the softened plastic to flow from the injection nozzle into the die cavities in which the plastic articles are

formed. The plastic flow first passes into the sprue which connects the nozzle of the heating cylinder with the channel or runner which leads to the mold cavity. At the extreme end of the sprue, a well is provided to entrap the first rush of plastic into the mold. Because this portion of softened plastic may be at a lower temperature than that recommended for flow, it is caught in the well and thus prevented from entering the mold proper. This well or trap is known, therefore, as the cold slug. From the sprue, the plastic flows through a series of *runners* into the individual cavities. The opening from the runner into the mold cavity is called the *gate*. In all cases, the size and position of the sprue, runners, and gate must be commensurate with the ease of flow of the plastic. The latter is dependent upon plasticity-temperature relationships. The total volume of cavity which must be filled by the piston stroke in injection molding is carefully regulated. Upon such a factor the proper dimensions of the mold

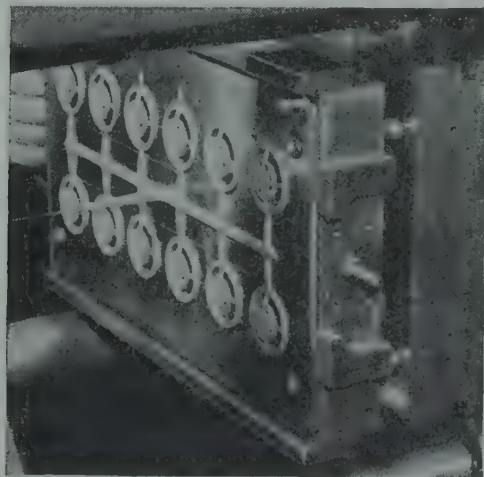


FIG. 22.11. Injection molded guards for gas mask valves. (Courtesy of Ideal Plastics Corporation.)

cavity parts and the number of individual cavities filled by each "shot" must be calculated. The portions in which flow is involved must be placed in such a way as to eliminate, as much as possible, uneven flow, weld lines, and unnecessary machining. A diagram which shows the essential parts of an injection molding machine is shown on page 420. Figure 22.11 represents the opening of an injection mold used to make guards for gas mask valves. This figure shows the sprue, the runners and the molded form produced.

Transfer Molds.—The design of a transfer mold is essentially the same as that for a compression mold. The important difference is that a transfer mold contains a cylinder in which the thermosetting resin is liquefied under pressure when the mold is closed and the fluid resin is then forced into the mold under pressure. Proper pressure and temperature are maintained until the cure is complete. Since the resin enters the mold in the fluid state rather than the solid state, as in compression molding, there is much less danger of breaking inserts.

Consequently transfer molding finds many uses in the manufacture of thermosetting plastic types in intricate shapes containing inserts.

Review Questions

1. What rules of product design may be stated in reference to each of the following:

Metal inserts
Wall thickness
Tolerances
Undercuts
Taper.

2. Illustrate by a diagrammatic sketch each of the following types of compression molds:

Positive
Semi-positive
Flash.

3. How can a mold be manufactured?

4. Illustrate diagrammatically the following parts of an injection mold:

Sprue
Runners
Ejection pins
Molded part.

CHAPTER XXIII

CASTING

Casting of plastics is similar to that of metals. In substance, the process consists of hardening a liquid resin while it is maintained in a mold form. The use of casting methods in the plastics industry is of less general interest than the use of molding. Production by this fabrication procedure is, however, particularly recommended for the formation of custom made forms or for low volume production. Such pre-fabricated shapes as rods, sheets and tubes are typical of the type of product formed by this process. In the discussion of resinous types in Section II, mention was made of the types of plastics used in casting. Phenolics are the most widely used resins in casting procedures and consequently, the major portion of the discussion is concerned with them. Ureas are rarely applied because of excessive shrinkage. In the thermoplastic field, casting of monomeric styrene or methyl methacrylate is often employed. A description of the casting process as applied to phenolics involves (1) the production of the resin, (2) the formation of the molds, (3) curing the resin, (4) finishing the cast object.

Production of resin: The phenolic resin is prepared according to the directions outlined (p. 171) for a one-step resin. Since one of the great advantages of cast phenolics is their translucency or colorability, particular attention must be paid to purity of reagents and control of experimental conditions. The condensation reaction is carried to the formation of a fusible resin which may then be dried, stabilized, and compounded with dyes, pigments, or lubricants.

Formation of molds: Casting molds are conveniently formed from lead. A steel arbor or master mold machined to the design desired is dipped into a molten bath of lead. After removal, a lead shell surrounds the steel arbor and when this is stripped off, a lead cavity or mold results. With suitable reinforcement this may be used once, remelted, and reshaped. Figure 23.1 is a picture showing the removal of a steel arbor from the molten lead bath. When molds are made from rubber, the designed model may be coated with a film of rubber by dipping into rubber latex or a rubber solution. When a film of sufficient thickness has been built up by repeated dippings, this may be stripped off and used as a mold form after reinforcement with

plaster. The operation might work in the opposite way if it is more convenient to duplicate the desired shape by shaping an outside periphery of plaster first. The interior surface of the plaster may then be smoothed by coating with rubber.

Since formation of a casting mold by such dipping processes involves stripping a one-piece shell from a mold form, it is important, in such cases, that undercuts or complicated designs should be eliminated. A *straight-draw* mold is, therefore, the most desirable type. Designs such as flutings, beads, and scallops must run in the direction in which the casting will be removed from the mold. When undercuts are necessary a *split mold* is used. These are produced from lead by die-casting. They are constructed in such a way that

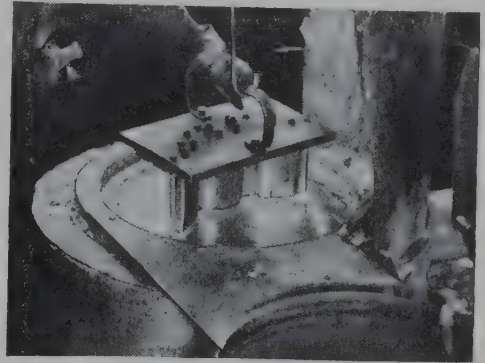


FIG. 23.1. The lead molds for casting catalin are formed by dipping the master steel arbor into molten lead. The lead freezes around the arbor and is stripped off to form the negative mold. (Courtesy of Catalin Corporation.)

opposite faces of neighboring molds are interlocked back-to-back. Assembly of the mold forms for curing of the resin is thus facilitated. The two-piece mold is closed at all points except that at which the resin is added, i.e., the gate. The main provision in the design of a

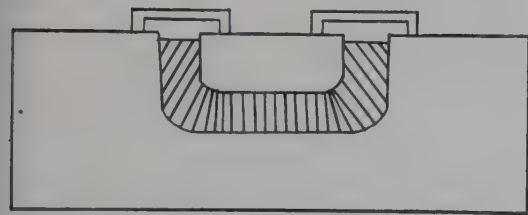


FIG. 23.2. Cross-section diagram of a cored mold.

piece to be fabricated from this type of mold is that the undercuts should be in not more than two directions. When the mold is opened, each half of the mold should be removable. In the manufacture of hollow, half-spherical pieces, a *cored mold* (Figure 23.2) may be used. The outer portion of this mold is made of

lead and is shaped to form the outside wall of the hollow casting being manufactured. Centered within the cavity of the external lead mold a metal core may be placed. This core is suspended in such a way that when the space between the mold and core is filled, a shaped article of the proper dimensions and design will be produced. Figure 23.3 is a loud speaker housing which is an example of a hollow casting.

Design of a casting mold is based upon certain fundamental factors. A minimum wall thickness recommended for cast articles is $3/16$ inch or, for very small pieces, $1/8$ inch. On the other hand, there is no great limitation of permissible wall thickness or size of a casting. The long curing schedules permit even curing throughout a large assembly. When straight-draw or split molds are used, a

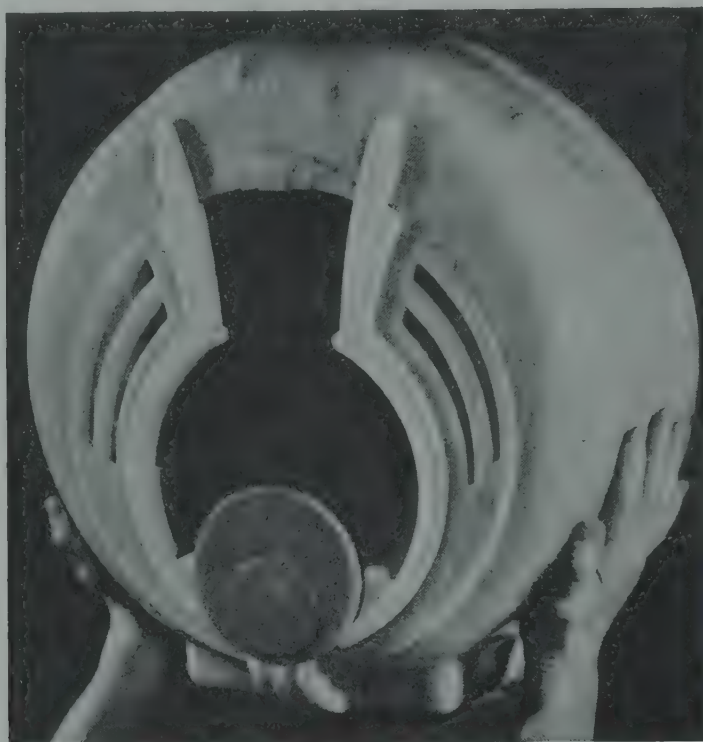


FIG. 23.3. Hollow casting produced in cored mold.
(Courtesy of Catalin Corporation.)

taper of .0015 inch should be provided to prevent formation of a vacuum, to reduce friction, and thus facilitate removal from the mold. Design of the piece should, wherever possible, allow for dimensional changes in the plastic piece, for changes as high as 1% are often encountered. For example, oversized holes for fastenings should be drilled and rigid bonding to other surfaces avoided because of differences in expansion values.

Curing: Hardening of the liquid phenolic resin takes place slowly at temperatures of approximately 80°C . The speed of hardening is, however, greatly altered by modifying either the type or amount of catalyst present. Too rapid hardening, or insufficient fluidity at the beginning of the process may result in poor castings, for entrapped air bubbles may be permanently occluded. One of the early diffi-

culties encountered in the use of *split* or *cored* molds was the tendency of the undercut parts of the designed shape to prevent the rise of air bubbles to the surface of the casting. The difficulty was eliminated by regulation of the initial viscosity and curing rate of the resin used.

An interesting modification of the simple curing process is one which is often applied to the manufacture of cast sheets. The liquid resin is cast into large blocks and these, in turn, are partially cured until a gum-like, pliable consistency is reached. These are then sliced and the thin sheets cured to completion.

Finishing: The main advantage of the cast shapes is the fact that a great variety of machining and fabricating operations may be used with them. Parts may be cemented together by the use of a liquid phenolic adhesive. Bending and shaping are possible after pre-softening in hot water. Such machining methods as drilling, lathing, threading, carving, sanding, and sawing are commonly used. Final polishing is done by buffing and wet or dry tumbling.

The versatility of the casting process is, therefore, appreciable. The colorability of cast phenolics, low cost for small volume production, ease of fabrication processes, and uniform curing of large pieces are factors responsible for its continued use.

Slush Molding.—A cold curing phenolic resin may be slushed about the walls of a rubber mold until curing takes place. This process, known as slush molding, results in the formation of a hollow cast object. Common articles or objects of art may be duplicated by coating with rubber and using this film, after removal, as the interior surface of a mold. A liquid phenolic resin, adjusted to rapid curing conditions by the addition of a mineral acid, may then be slushed in the interior of the mold until curing takes place. A typical curing period is fifteen minutes. The hollow object, a replica of the original which was coated with rubber, is then obtained when the mold is broken away. Careful adjustment of the acid content is necessary in order to prevent injurious effects on the dyes present and poor stability on aging of the plastic.

Thermoplastic Castings.—In the thermoplastic field, casting of methyl methacrylate and styrene are of particular interest. Both of these types are noted for their light weight and optical clarity. The latter property is combined with improved heat resistance when the raw materials in either the monomeric or partially polymerized form are cast and hardened. In the case of the methacrylate, a common method is polymerization of the monomer while in a shaped mold. The inhibitor-free monomer may be polymerized under the

influence of heat, light, and oxygen. The reaction is strongly exothermic even at the usual temperatures of below 40° C. Careful control of temperature and facilities for the dissipation of heat must be provided in order to prevent the formation of bubbles of gas arising from the local decomposition of the monomer or resin. Faster casting cycles are possible by the use of partially polymerized methacrylate and benzoyl peroxide as the catalyst.

Hardening starts at the bottom and proceeds toward the top when columns of monomer are being polymerized. Cast sheets for use in aircraft (p. 247) are valuable because of their adaptability to shaping. Methacrylates are used in dentures prepared by a casting method. In both cases, the excessive shrinkage during polymerization (sometimes as high as 20%) may be objectionable. The amount of shrinkage can be decreased to some extent by starting with a solution of the completely polymerized methyl methacrylate



FIG. 23.4. Cast polystyrene. (Courtesy of The Dow Chemical Company.)

dissolved in the monomer instead of the liquid monomer itself. The fineness of detail that can be reproduced by a casting process is illustrated in Figure 23.4.

Styrene may be separated from inhibitor, partially polymerized, and cast by means of a continuation of the polymerization reaction.

See Figure 23.4. Heating, preferably in the absence of oxygen, at 100–135° C. causes final hardening. Excessive shrinkage, bubble formation, and yellowing are difficulties which must be guarded against and avoided.

Review Questions

1. Describe the formation of a mold used for casting.
2. What is meant by:
 - (a) straight draw
 - (b) cored mold?
3. Describe the process of slush molding.

CHAPTER XXIV

LAMINATING

The process of laminating has increased in importance to the point where it now rivals molding in popularity and low cost. Fundamentally, the technique is one of impregnation of a porous sheet filler, followed by shaping and compressing of the stacked sheets. In the final steps, the laminate is subjected to heat and pressure simultaneously. The process is comparable, therefore, to the process of compression molding. As in the latter case, thermosetting resins are commonly used. Occasionally, a thermoplastic type—particularly the vinyl resins—may be applied. The difference in properties of the two principal types of thermosetting resins accounts for the classification of laminates into *Industrial* and *Decorative* types. The phenolics, characterized by their relatively poor colorability but excellent strength, act as the resin base for the industrial laminates. The ureas are of greater usefulness in the decorative field because of their excellent colorability and surface hardness, even though they have less mechanical strength than the phenolics. The melamines also find wide application for decorative purposes and for uses in which electrical properties are of importance. Thus, the phenolics are commonly encountered in laminated gears, cams, motor housings, fan blades, and spinning buckets for rayon manufacture. The ureas and melamines are found in decorative table tops, wall paneling, inlaid murals, advertising displays, refrigerator panels, Venetian blinds and light fixtures.

The resin is applied to the porous sheet filler in the form of a varnish using alcohol, water or a mixture of these as the solvent. Regulation of the viscosity and solids content of this impregnating liquor is one of the first problems of the laminator. The viscosity must be low enough to provide for ample impregnation of the filler, but the solids content must not be reduced to a point where insufficient solid resin is left in the filler. The ratio of resin to filler which produces the optimum properties must be determined by trial and error. If insufficient resin is present, poor adhesion of the laminate plies and a reduction of the mechanical strength will result. The quality of the filler must also be carefully controlled to insure that the same degree of impregnation is always obtained. Control of the

porosity, fiber count, density, thickness, acidity or alkalinity, color, and purity is maintained. The resin content in the filler may be varied between the wide limits of 20 to 70% of the total.

Impregnation may be carried out in several ways. The most common method is immersion of the filler in a dip tank containing the resin varnish and is illustrated in Figure 24.1. Absorption of the

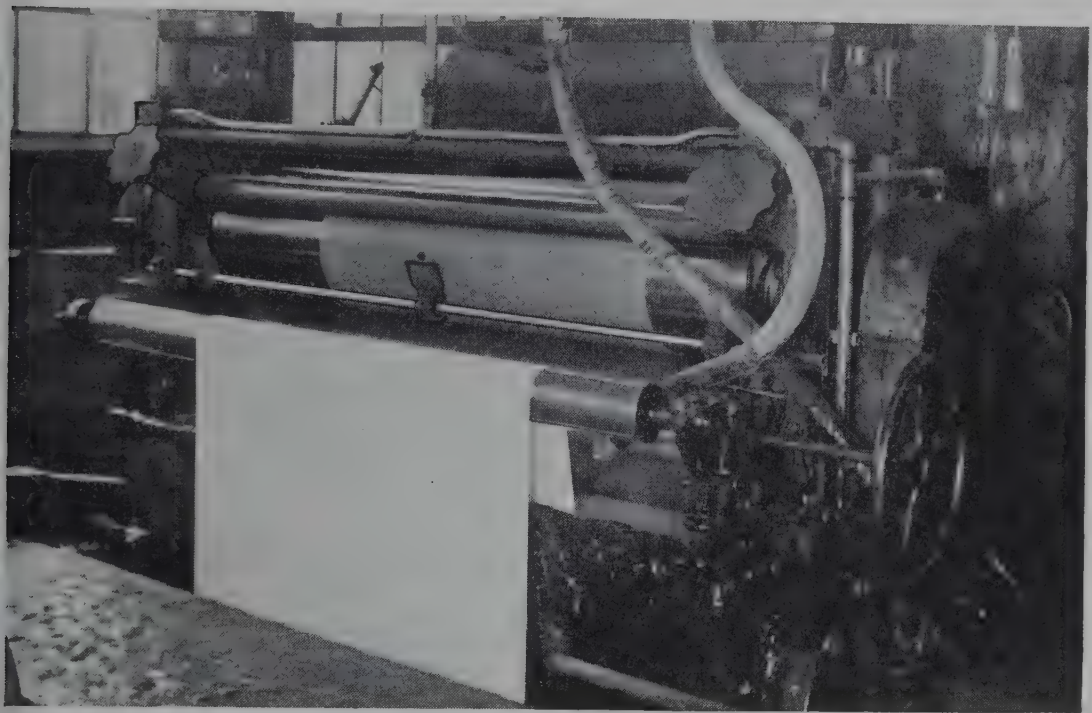


FIG. 24.1. Paper stock being impregnated prior to laminating.
(Courtesy of General Electric Company.)

varnish occurs and the excess is scraped off by adjusted knife blades. Coating rolls which pick up the varnish from a tank and carry it onto the filler may be used. The amount of material deposited may be controlled by variation of the distance between rolls or by passing the filler between knife blades which scrape off any excess. In rarer cases the resin film is merely deposited on the surface of the sheets to be laminated. Wood veneer, for example, is often laminated by such technique. Spreading of the resin varnish on one side of the filler deposits a film of bonding resin. Adhesion of the plies depends on partial absorption of the fluid resin by the untreated side of the next ply and the natural adhesion of the resin to the filler.

After impregnation, the volatile constituents of the varnish are driven off by passing the filler through a heated chamber or tower. Steam coils or hot air can be used to dry the filler to the desired

liquid content. A small portion of the solvent is allowed to remain in the sheet in order to facilitate final shaping. The combined resin-filler is now ready for shaping and curing. The operations from this point will depend upon the shape which is desired.

Most of the laminated structures which are produced commercially are produced from simple shapes. The pre-fabricated forms include sheets, rods, and tubes. The assembly is built by piling sheets of the desired size upon one another. (See Figure 24.2.) The thickness

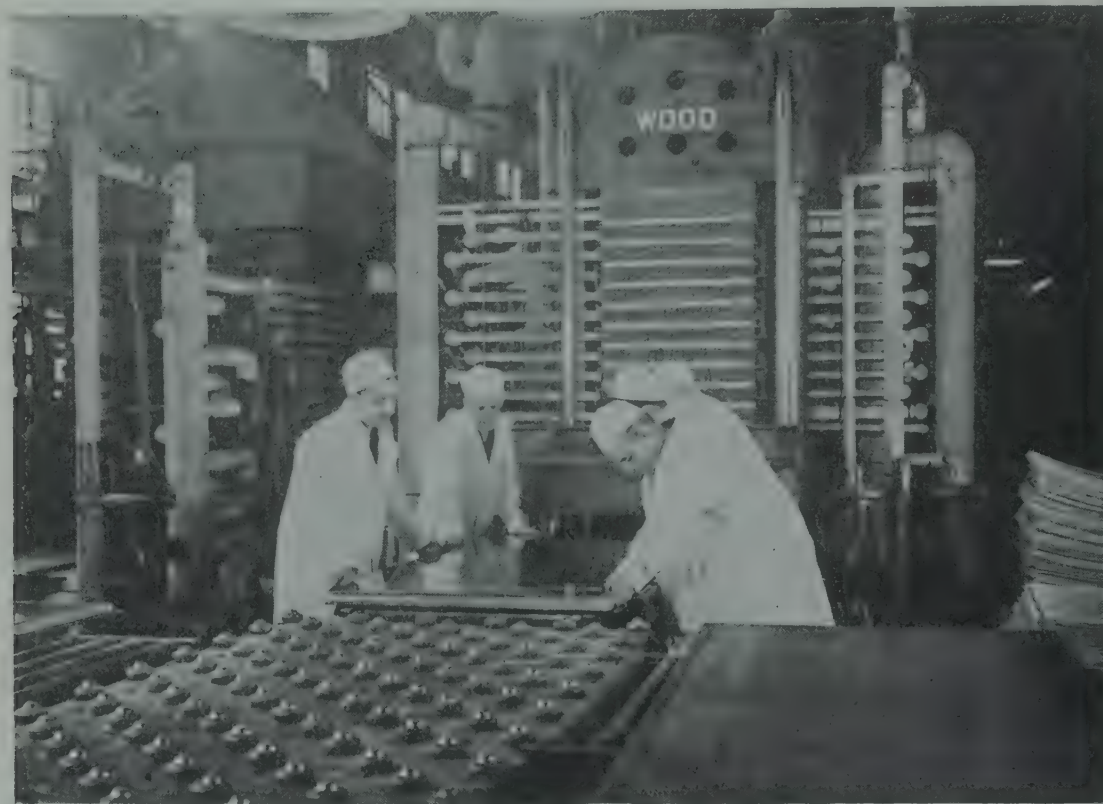


FIG. 24.2. Assembling impregnated sheets. Multiplaten press is shown in background. (Courtesy of General Electric Company.)

of the product depends upon the number of sheets used. It is often found advantageous to vary the composition of the laminating plies. Thus, the core of a decorative laminate may be built up using a phenolic of poor colorability. The surface sheets, however, contain urea resin and the coloring effect is easily obtained. The resin content of the surface sheets may be higher than that of the core sheets in order to improve the hardness, strength, or electrical resistance at the surface. The assembled structure is placed between heated plates of a press—preferably of a multiplaten type—and

subjected to heat and pressure until curing is complete. The pressures used range from 1000 lbs. per sq. in. to 3000 lbs. per sq. in., the temperature may vary from 132°C. to 160°C. ($270\text{--}320^{\circ}\text{F.}$), and the curing cycle may be from 30 minutes to several hours. The conditions necessary in each case will depend not only on the type of resin being processed but also upon the dimensions of the sheet being formed, density desired, and the ratio of resin to filler. Fabrication of the cured laminate is completed by simple machining operations. The rough edges are trimmed, the surface is polished by buffing, and the final shapes may be produced by sawing, pressing, drilling, printing, etc.

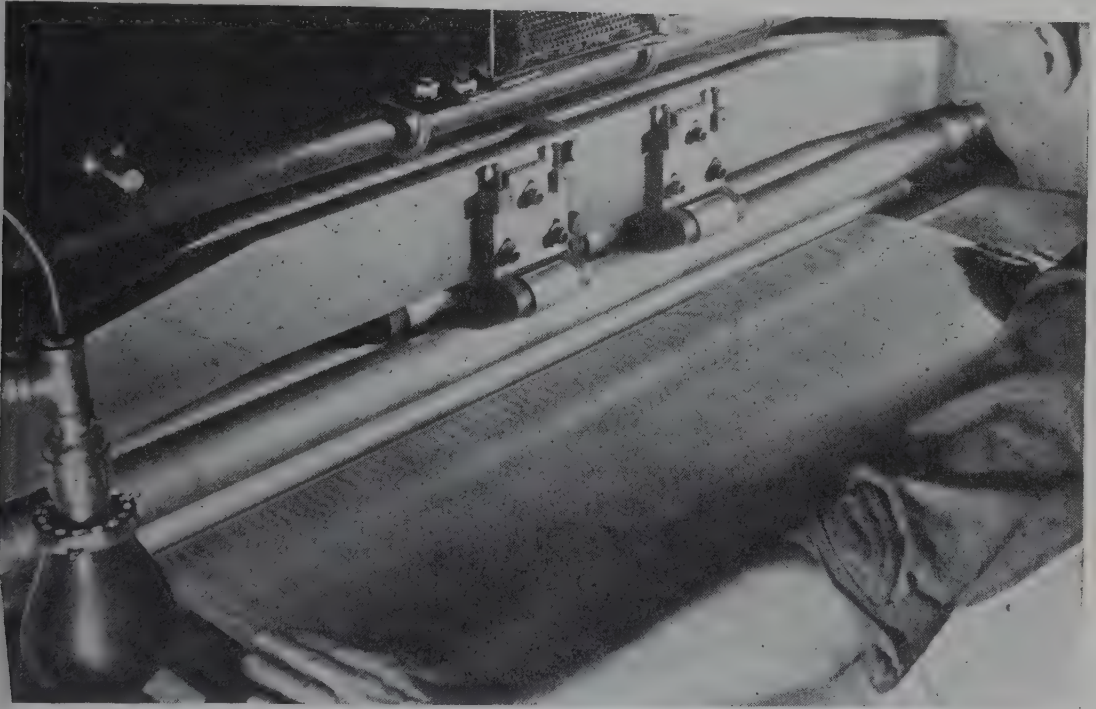


FIG. 24.3. Rolling resin-impregnated paper on a mandrel.
(Courtesy of General Electric Company.)

Laminated tubes are formed by wrapping the impregnated filler around a mandrel and curing. "Rolled tubing" results from a process which provides for rolling with the simultaneous application of heat and pressure, as shown in Figure 24.3. The resin in the filler is softened by heat and, while wrapping, the layers of the roll are bonded together by pressure. These assemblies may then be cured in an oven and machined to the desired dimensions. "Molded tubing" is manufactured simply by wrapping the filler around a mandrel and curing the assembly in a mold. Laminated tubes

measuring 6 feet in diameter and 8 feet in length are used in power transformers. Laminated rods result from wrapping of the resin-filler about a mandrel of small diameter and removal of the mandrel before curing in a mold. The desired diameter is then produced by grinding, and the finishing is completed by buffing or applying a lacquer.

Fillers.—The fundamental difference between the filler of a molding powder and a filler of the laminating process is that the latter is of a continuous nature. The two types are comparable except for the fact that in molding we use a disintegrated or shredded powdery material whereas in laminating a continuous sheet is used. The most important types of fillers will be discussed.

Paper: Special types of high absorptive power are used in laminating. Rag paper is characterized by its great toughness. Its high cost, however, prevents it from being used in many cases. Kraft paper is most generally used because of its low cost and satisfactory mechanical properties. Paper made from alpha cellulose is chosen for applications requiring colorability, uniformity of appearance, and good electrical properties.

Fabric: A variety of fabric bases may be used in laminating. Such types of fabric as canvas, army duck, twill, airplane cloth, herringbone weave, and organdy are commonly used. The chief controlling factors are those of weave and weight. In most cases the proper laminate may be prepared by the use of fabrics weighing 3–18 ounces per square yard. For some heavy duty applications, however, fabrics weighing up to 40 ounces per square yard have been used. An example of such a product is the bearing used in steel rolling mills. Of equal importance, however, is the weave of the fabric. If the thread counts in longitudinal and lateral directions differ, the strength of the laminate will depend upon the direction of testing. In general, the closer the weave of the fabric the greater will be the tensile and impact strengths of the finished product. Most fabrics are of standard make and are provided in an unsized, unbleached condition unless otherwise specified. The improved mechanical properties obtained with the proper fabric base permit the extension of laminates to a variety of applications in the industrial field for which the older molded resins are unsuitable. Cams, gears, bearings and motor parts are representative of the industrial possibilities.

Asbestos: Asbestos is provided for use in laminating in the forms of a paper or fabric. The latter, of course, insures greater strength, but both types exhibit good heat resistance and good chemical

resistance to corrosive agents. Greater moisture resistance and electrical resistance are also provided by the asbestos cloth.

Glass: A glass cloth, Fiberglas, made of staple-fiber yarn produces a laminate of excellent resistance to impact, heat, and moisture. In the electrical industry this filler is popular for insulation combined with heat resistance. The use of staple-fibers produces a cloth containing many small strands. Recent developments in the use of glass-reinforced plastics are described in *Modern Plastics*, 21, (9), 89-113 (1944).

Wood: Wood veneers are commonly laminated to produce structures of unusual strength. These products are generally considered as *plywood*. A differentiation between *laminated* wood and normal plywood has been made on the basis of the method of assembly. Laminated wood is reserved for those structures in which the fiber direction of all plies is unchanged. Normal plywood is used to refer to those in which the fiber direction is crossed in alternate plies.

DECORATIVE LAMINATES

Laminates which owe their popularity to decorative characteristics are termed "decorative laminates." They are broadly divisible into *opaque* and *translucent* types. The former exhibits great depth of color and stability of color when the surface sheets are made by the use of a urea resin. The core, even in such cases, may be made of a phenolic resin. The translucent types are made of urea resin throughout. The color is introduced by ball-milling a pigment into the resin varnish used for impregnation. Often, a core sheet may be selectively colored to produce a design or lettering effect. The use of decorative laminates is a broad one. Wall paneling, lamps, translucent shades, indirect lighting, name plates, counter tops, automotive interior trim, and furniture are several typical applications.

The versatility of decorative laminates is illustrated by the unique possibilities which may be obtained. A glossy, satin, or Morocco finish is easily produced. Mahogany, marble or walnut surfaces may be printed. Inlays are produced by using a design cut out of an uncured sheet of different color or using a shaped design of impregnated wood. Metal inlays are also used. The surface may be printed or engraved by using inks compounded from phenolic or urea resins. Metal foil may be inserted immediately below the surface to conduct heat from the surface and thus prevent burning or blistering from a lighted cigarette. Printed fabrics may be used at the surface to produce any desired pattern.

An increase in the use of fluorescent dyes has resulted in fluorescent effects in the laminated structures. Instrument panels may be conveniently prepared and lettered in this way.

General properties exhibited by this type of laminate make them valuable for long service. Hardness, abrasion resistance, chemical inertness to fruit juices and mild alkalis, dimensional stability and mechanical strength are properties which have contributed to the usefulness of these laminates.

INDUSTRIAL LAMINATES

Laminates were first introduced into industrial service because of the opportunities they offered of providing electrical insulation combined with high strength and light weight. It is not surprising to find, therefore, that the growth of the laminates has paralleled that of the electrical, telephone, and radio fields. Thin, easily fabricated sections are used in the lighting and ignition systems of motors. Switchboards are insulated with laminated punchings, and



FIG. 24.4. G-E textolite rayon spinning bucket, wire reinforced.
(Courtesy of General Electric Company.)

relays, cut-offs, control units and induction coils all make use of the electrical stability of this construction. The high dielectric strength is necessary for the application of laminates in X-ray and therapeutic

equipment, transformer tubes and condensers. It is found that in many cases the laminated structure may be machined or shaped at less cost than that required for a molded product. The ease of machining and fabrication is evidenced by the multitude of small, punched machine parts made of laminated sheet stock. Laminated

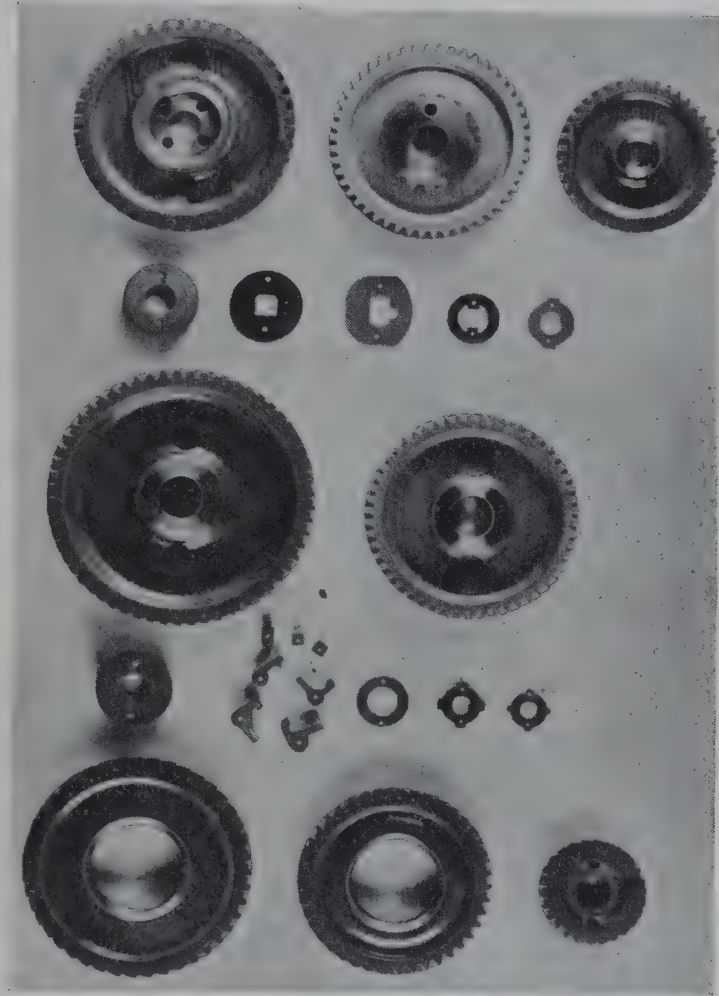


FIG. 24.5. A group of laminated plastic automotive parts, including timing gears, cam gears, distributor breaker arms, magneto couplings, and insulating washers. (Courtesy of Bakelite Corporation.)

products are sometimes shaped and then cured by subjecting them to ordinary compression molding. This treatment is practical if the shape of the object is not too complex. Industrial protective helmets, fan blades and serving trays are typical of molded laminates. Figures 24.4, 24.5 and 24.6 illustrate some industrially important laminated articles.

In applications which emphasize mechanical strength rather than electrical resistance, the fabric base laminates are particularly valuable because of their combination of high strength and low

weight. Laminated gears, bearings, retainer rings, rotor vanes, and motor housings may be readily machined from stock shapes. The net effect in such applications is elimination of noise, elimination of lubrication difficulties, (water is used as a lubricant) and resistance to corrosive materials.

LOW-PRESSURE LAMINATING

Because of its ease of operation for the formation of curved and intricate laminates, low pressure laminating is widely used at the present time in many commercial processes. Fundamentally, the technique consists of bonding the common fillers—fabric, paper and wood—by the use of phenolic, urea, melamine or, in rare cases,

thermoplastic resins. The distinctive feature is the fact that low pressures and low temperatures are used for the curing. By the application of “fluid pressure” as in flexible rubber bag molding, unusual shapes and curvatures may be formed readily. Inflation of the bag by steam or air or evacuation of the bag causes it to create pressure against any desired contours. The technique is commonly referred to as the Vidal, Duramold or Timm process.

In high-pressure laminating, pressures of 1500–2000 pounds per square inch and temperatures of approximately 150° C. (300° F.) are applied. In low-pressure laminating, however, the pressure rarely exceeds 300 pounds per square inch and, although the curing temperature is directly dependent upon the type of resin adhesive being used, it is usually maintained below 65° C. (150° F.). Because of these basic differences existing between the two techniques, the cure or hardening of the resin must be carefully regulated. A “cold-setting”



FIG. 24.6. Molded laminate fan blade. (Courtesy of General Electric Company.)

adhesive resin may be prepared from a phenolic or urea base by the addition of a strong catalyst. Strong acids or materials capable of forming acidic catalysts by the addition of water are commonly used. Although such adhesive resins are properly termed "cold setting," their cure is advanced and their general properties are enhanced by a short baking schedule at low temperatures. Convenient methods of packaging such adhesive resins are represented by the two-part or water soluble adhesives now sold. In one commercial preparation, the resin and catalyst are stored in separate containers and mixed immediately prior to use. In another preparation the dry resin powder and the solid catalytic agent are stored in the same container. When water is added to this mixture, the aqueous solution of the acid catalyst causes the curing of the resin.

When higher temperatures may be used, as in the formation of plywood, and the application of pressure by weights or presses rather than by a flexible bag is possible, a heat-setting adhesive resin for use at temperatures of approximately 150° C. (300° F.) for phenolic types and 107–141° C. (225–285° F.) for urea or melamine types may be used. A convenient method of fabricating the adhesive resin is in the form of a resin film or resin deposited on fine paper. When either of these types is used, there is, of course, no impregnation of the material being bonded prior to the assembly and curing. In the case of a thermoplastic resin, as the vinyl type, the laminates may be assembled while there is sufficient residual solvent to produce adherence of the plies or, at higher temperatures, the plies will adhere as the thermoplastic resin softens and flows between plies. When a thermosetting adhesive resin is used, it is incorporated in the assembly while still in the fusible state. On the application of heat and pressure to the assembly, the resin flows and impregnates the plies before hardening to the infusible state.

The fillers used in this process are similar to those applied to laminating at high pressures. Paper, fabric, or asbestos are often used in order to obtain specific properties. Paper or fabric facilitates the formation of curved structures. Compound curves are readily obtained by impregnation of the filler and adjustment of the resin content to 35–50% of the sheeting. Flexibility and deformability are regulated by the amount of volatile component left from the drying ovens, the characteristics of the filler, and the resin-filler ratio. The major difficulties encountered when using fabric or asbestos are concerned with the degree of bonding between plies, the decreased strength obtained as compared to high pressure laminates, and the increased moisture absorption if a low resin content is

used. Flexibility is often sacrificed by increasing the resin content in order to improve moisture resistance.

Wood veneers are used as the sheet stock in the formation of plywood. The uniformity, strength, light weight, and ease of fabrication of these products are responsible for the rapidly increasing popularity of these products. The veneers are formed by sawing or slicing sheets from large, steamed logs. The cutting method varies according to the type of design being produced and the construction necessary. Some sheets are cut in a rotary process by slicing a continuous sheet from the circumference of the log, some are sliced in a half-round fashion by cutting along the outside surface of one face and others are simply sliced by longitudinal cutting of the log. In all cases, however, the retention of the grain and the decorative effects which may result from its use must be considered. Different types of wood may be used and allowance must be made for variability of porosity by adjusting the amount of bonding resin used or the method of application. The moisture content, however, must be carefully regulated within narrow limits. Values of 5-6% are preferred, though lower or higher moisture contents are desirable in certain applications.

When the bonding resins are applied to the surface of the veneer, the degree of impregnation is directly dependent upon the viscosity of the resin adhesive used. It should be emphasized that the degree of impregnation of the resin into the wood is not nearly as great as the impregnation of more porous materials such as paper and cloth. The resin acts principally as a bonding agent for the adhesion of the wood veneers, and usually amounts to only 6% of the total weight of the plywood. The simplest method, when possible, is the use of a solid resin film as the bonding agent. In other cases, the surface of the veneer is spread with a solution of the resin. When hard woods are used, a single spread coat, applied to one surface only, may be sufficient to produce bonded strength. Soft, porous, or dry woods, however, require greater quantities of resin and double spreading, i.e., spreading on both surfaces, in order to obtain sufficient bonding between plies. Even under these conditions, a preliminary conditioning by coating with a dilute solution of the resin may be necessary. After regulation of the volatile content according to the degree of deformability desired, the veneers are assembled into the shape being produced. Curvatures and complex designs are readily obtained by the use of properly cut veneers. Crossing of the grain is necessary for maximum resistance to distortion and warpage. The

construction will, however, depend upon the strength requirements of the finished product.

Final curing of the assembled piece is completed by any convenient method of applying heat and pressure simultaneously. Flat sheets are easily cured in a simple hydraulic press using heated platens. The difficulty of transferring heat to the inner plies by the use of this method without scorching the outer plies has led to the use of protective cauls and to the development of dielectric heating in a high

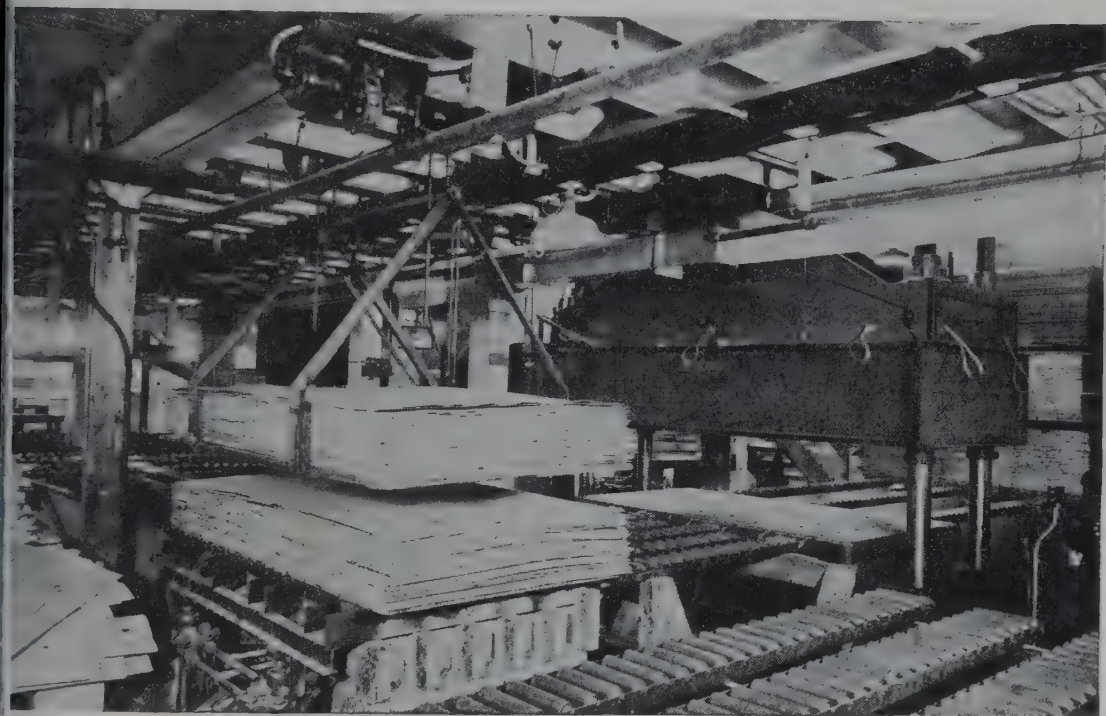


FIG. 24.7. Assembly of plywood panels. Note position of center electrode between the plywood stacks. (Courtesy of The Girdler Corporation.)

frequency electric field. This method of heating is the same as that used in heatronic molding described in Chapter XXI. The distinctive feature of this process is the fact that heat is developed *within* the stacked veneers, thus permitting the formation of thicker sections in a much shorter period of time. At the same time, over-curing and scorching of the top surfaces are effectively eliminated and a more uniform product results. Figure 24.7 shows two piles of plywood panels which have been treated with resin and are being assembled prior to placing in a hydraulic press, while Figure 24.8 shows the plywood panels, together with the center electrode in the hydraulic press, being heated by the high frequency method. With a center electrode, the top and bottom parts of the press can serve

as the other electrode, thus solving the problem of insulating the electrodes.¹ The saving of time which can be achieved by high-frequency heating is illustrated by the fact that laminated aircraft spars which formerly required eight hours of heating with steam can now be produced in twenty minutes.²

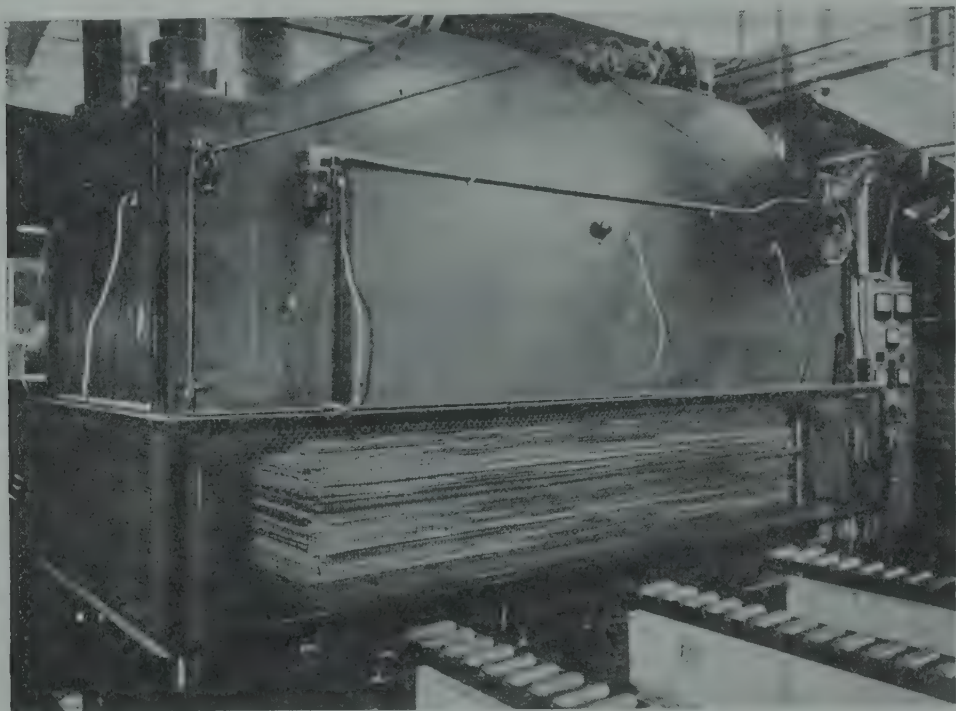


FIG. 24.8. High-frequency heating of plywood panels in hydraulic press. (Courtesy of The Girdler Corporation.)

A novel and interesting method of applying radio-frequency power has been developed for the spot-gluing of thin strips of veneer in the making of curved articles from plywood. The usual process of making such articles consists in fastening a thin sheet of glue-coated veneer to the mandrel by means of wire staples. As successive layers are forced into position and fastened to the mandrel, the wire staples must be removed from the preceding layers. In the new method,³ the wire stapler is replaced with a radio-frequency (r-f) gun consisting of inner and outer coaxial electrodes, separated by a suitable insulating medium. A frequency of 200 megacycles is used and the heating effect extends about 1/16 inch beyond the end of the gun, over an area approximately equal to that of the inner electrode.

¹ Taylor, *Trans. Am. Soc. Mech. Eng.* **65**, 208 (1943).

² Taylor, *Electronics*, **17** (1), 96 (1944).

³ Taylor, *Electronics*, **16** (11), 106 (1943).

Since the resins generally used as adhesives for this work (phenol-formaldehyde and urea-formaldehyde resins) are thermosetting, it is desirable to apply the heat only long enough for the resin to reach a thermoplastic state so that, on cooling, the plies will stick together. If excessive heating of the resin occurs, the flow of the resin when subjected to the curing operation may be reduced to such a point that poor bonding is obtained. If proper flow is maintained when the whole assembly is heated under uniform pressure, all of the resin, including the "tacked" portions, becomes plastic and the plies are free to move slightly, if necessary, in order to assume the desired shape.

The advantages of the r-f gun over the wire stapling method are:

1. Saving of time due to the fact that there are no staples to be removed.
2. Elimination of holes in the veneers.
3. More uniform product, due to ability of plies to acquire desired shape when heated under pressure.

Low pressures are easily reached by the use of clamps, weights, nailed strips, etc. If care is taken to provide for uniform pressure, any suitable device may be applied. Probably the most common procedure in the field of laminating, and particularly for the production of curved or irregular plywood assemblies, is the use of a flexible bag and "fluid pressure" by expansion or evacuation against a molded form. By this means, even pressure is exerted in all directions and difficulties due to variations of veneer thickness are eliminated. The bags are fabricated from rubber sheeting or rubber-coated fabric. Any rubber-like or strong sheet material which will withstand the pressures and temperatures to be used may replace the rubber. The thickness of the sheeting must be chosen to meet requirements of abrasion resistance and strength, but the thickness or stiffness should not detract from its ability to transfer heat or its adjustability to designed contours. The bag is fabricated into the most suitable shape from the sheet stock and the parts cemented and reinforced. Vents are provided for the passage of air or steam.

The three common methods of applying fluid pressure of this type have been summarized by Perry ⁴:

- a. Inflatable closed bag or mattress not containing the plywood,
- b. Deflatable open-end bag containing the plywood,
- c. Deflatable half-bag, or blanket enclosing the plywood in which the mold constitutes the other half of the bag."

⁴ Perry, *Modern Plastics*, 20 (12), 74 (1943).

These three types are diagrammatically illustrated in Figure 24.9. Figure 24.9A shows the assembled plies on a wooden or metallic mold and the inflated bag being pressed between the surface of these plies and the retaining wall of a chamber in which the assembly has

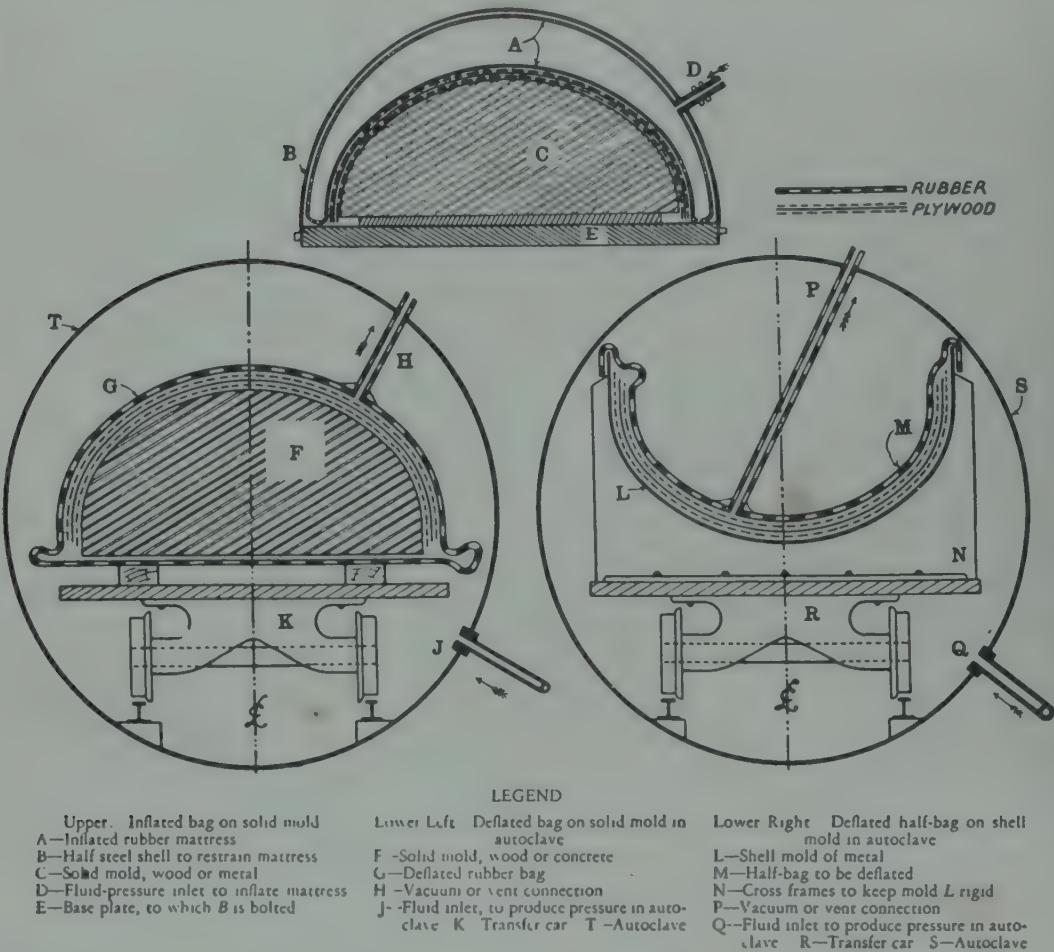


FIG. 24.9. Methods of applying fluid pressure (Parts separated to show detail more clearly.) (Perry, *Modern Plastics* 20 (12), 75, 1943.) (Courtesy of The Resinous Products and Chemical Company.)

been placed. Figure 24.9B shows the plywood and mold in an evacuated bag. Pressure is being exerted by the introduction of steam or hot air into the outside chamber. The arrangement in Figure 24.9C utilizes the same principle, but in this case, a half-bag or single sheet is fastened to the mold form. Figure 24.10 shows a fluid pressure assembly being placed in an autoclave to be cured.

The properties of the finished product depend upon several factors. The amount and properties of the bonding resin present, the type of

wood used, the pressure and temperature applied, the length of the curing cycle, and the construction of the laminate must all be considered. The effect of variation of laminating pressure upon the final tensile strength of cloth laminated with three different adhesive resins is shown in Figure 24.11. The term "aminoplast" refers to a urea-formaldehyde adhesive resin.

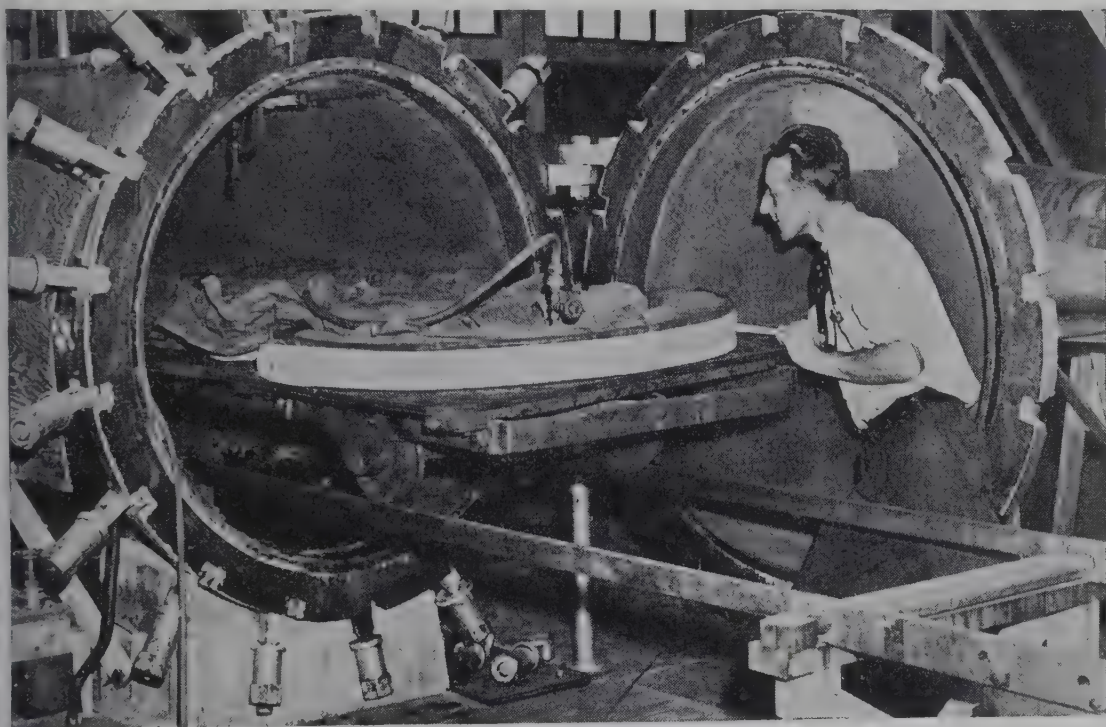


FIG. 24.10. Low pressure laminating. (Courtesy of The Resinous Products and Chemical Co.)

The fact that laminated products may now be conveniently prepared in curved shapes (Figure 24.12) has permitted rapid expansion into new and large-scale applications. The unusual strength, rigidity, variability of decorative effects, and excellent aging properties are responsible for its increasing use. Airplane fuselages, rudders, flaps, bomb doors, refrigerator paneling, railway car interiors, machine housings, bus bodies, boat hulls, automobile parts, and building constructions are several of the large scale products which may now be fabricated from low pressure laminates.

IMPREGNATED WOOD

The properties of wood can be improved substantially by impregnating it with an aqueous solution of a suitable resin. The most

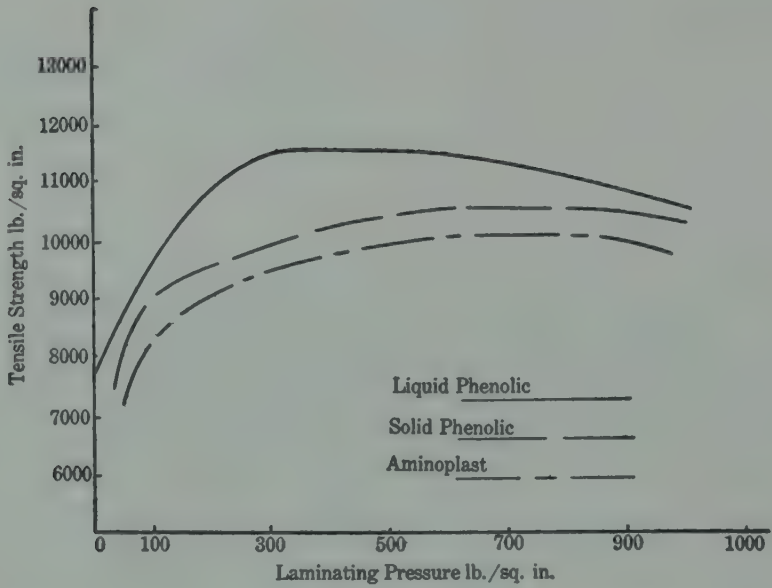


FIG. 24.11. Effect of laminating pressure upon tensile strength. (J. H. Du Bois *Plastics*, p. 370, American Technical Society, Publishers, Chicago, 1943.)



FIG. 24.12. Front view of aircraft pilot seat made from canvas fabric impregnated with a modified phenolic laminating varnish. (Courtesy of Capac Manufacturing Company.)

widely used resins are fairly low molecular weight, water-soluble phenolic resins. Although large pieces of wood can be impregnated, the process is generally applied to veneers. These are immersed in the resin bath and impregnation may be accelerated by applying pressure (usually 45–50 pounds per square inch) to the system. The absorption is usually continued until the resin content of the wood is 30–35%. The veneers are then dried and heated to 95–120° C. (200–250° F.) in order to cause polymerization of the resin in the wood to the insoluble, infusible state. These veneers are bonded together by the same procedures that are used for plywood or laminated wood. The wood is frequently called "Impreg" and has about the same density as the untreated wood.

The improvements in the properties of wood obtained by impregnation with resins have been summarized by Casselman.⁵ Resin-impregnated wood is harder, less permeable to moisture, more resistant to decay and the action of termites, and more brittle than untreated wood. Because of its moisture-resistance, resin-impregnated wood will retain its dimensions better than ordinary wood and will not shrink or expand as much under different conditions of humidity. "Impreg" can be used for any of the applications for which plywood is used. At present it is being used as the surface ply of parts used in making aircraft, boats and pontoons.

Compregnated wood, "Compreg," is made by curing resin-impregnated wood at high temperatures (127–160° C., or 260–320° F.) and high pressures (900–2800 lbs. per sq. in.) The resin, before it reaches the completely cured state, exerts a plasticizing effect on the wood, so that resin-impregnated wood can be compressed or densified to a greater extent than ordinary wood. Compregnated wood can be obtained having densities of 1.3–1.4. It possesses the same advantages as impregnated wood, but possesses them to a greater extent. As the density of "Compreg" increases, the hardness, tensile strength, compressive strength and modulus of elasticity also increase. Compregnated wood has been obtained with a surface hardness of 90% of that of plate glass. "Compreg" is used for making ski and sled runners, wooden parts where electrical insulation is desirable, and wooden blades for use as propellers and ventilating fans.

In the use of phenolics in combination with wood, three methods of treatment have been mentioned in this text and summarized by Klein, Grinsfelder, and Bailey⁶ as:

⁵ Casselman, *Modern Plastics*, 21 (3), 125 (1943).

⁶ Klein, Grinsfelder and Bailey, *Ind. Eng. Chem.* 36, 252 (1944).

1. Resin adhesive bonding as in plywood.
2. Use of resin in film form between plies of wood.
3. Impregnation followed by curing with heat and pressure.

The characteristics of wood treated by each of these three methods are given in Table I-24:

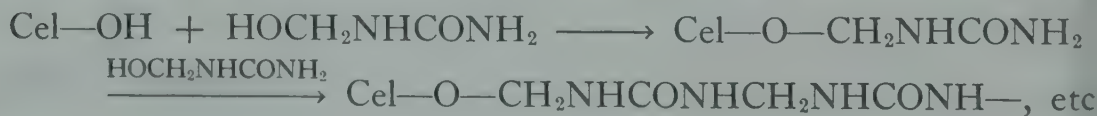
TABLE I-24. SUMMARY OF PROPERTIES RATED FOR TYPE OF IMPROVED WOOD

Property	Impreg- nated Process	Film- Bonding Process	Glue- Spreading Process
Simplicity and uniformity of production	3	1	2
Ease of compression	2	3	1 ^b
Dimensional stability			
Water	1	3	2
Heat	3	1	2
Impact strength	3	1	2
Tensile and compressive strength, moduli of rupture and of elasticity in bending	2	1	3 ^b
Shearing stress parallel to grain			
Perpendicular to laminations	2	1	3
Parallel to laminations	1	1	1
Machinability, glueability, paintability	3	1	2
Surface appearance	1	3	2

^a 1 = best; 2 = intermediate; 3 = poorest.

^b If a less alkaline resin were used, the ease of compression might have been somewhat less, but the compressive strength, modulus of rupture in bending and modulus of elasticity might have been appreciably higher as is indicated by data from other sources.

A most interesting development⁷ in the field of impregnated wood is the discovery that the hardness of wood can be improved materially by impregnating the wood with a solution of methylolurea, drying the wood, and subsequently heating it to cause polymerization of the methylolurea. The solution of methylolurea is usually made by dissolving 1-2 parts of urea and 6 parts of dimethylolurea in 20-24 parts of water. Such a solution would contain both methylolurea and dimethylolurea. It is believed that the cellulose in the wood reacts chemically with methylolurea to form a product which can react further with additional molecules of urea, e.g.,



⁷ *Chem. and Eng. News*, 22 (9), 726 (1944).

f some dimethylolurea enters into this condensation, cross-linkages become possible.

The actual process of impregnating the wood consists in evacuating the chamber in which the dried wood is placed, introducing sufficient solution so that the wood will be completely covered even after absorption is complete, and then allowing the absorption to occur at atmospheric or super-atmospheric pressure. For the impregnation of veneers up to 0.0625 inch thick, atmospheric pressure is adequate, but for the impregnation of larger pieces of lumber, higher pressures, 100 lbs. per sq. in. or more, are necessary. The treated wood is then dried either in kilns or by exposure to air. In either case, the reaction with cellulose and the condensation polymerization are believed to be catalyzed by the acids present in wood. If the treated wood is dried at a moderate temperature, the resin reaches an insoluble but still fusible state. Such wood can be heated to about 116° C. (240° F.) and compressed to form a harder wood than is obtained without subjecting it to pressure.

The outstanding characteristics of this type of treated wood are its hardness, low heat conductivity and resistance to moisture and chemicals. Table II-24 illustrates the improvement in hardness obtained by treating a few types of wood by this process. An increase in hardness is accompanied by an increase in brittleness, and strips of treated wood are stiffer than those of untreated wood.

The low heat conductivity of treated wood is shown by the fact that it takes twice as long for an oxy-acetylene torch flame to cut through a half-inch section of treated wood as to cut through a

TABLE II-24.^a HARDNESS ^b OF TREATED AND UNTREATED WOODS

	Untreated	Treated	Treated and Compressed
Ponderosa Pine	-10	50-60	125-130
Soft Maple	10-20	70-80	—
Hard Maple	40-60	70-100	—
Dogwood	70-80	100-125	—
Persimmon	70-80	—	—
Ebony	125-130	—	—
Balsa	—	—	185-190 (sp. gr. 1.3)
Aluminum	180	—	—

^a Private communication from J. F. T. Berliner, E. I. DuPont de Nemours and Co.

^b Values obtained by a modified Rockwell test using a 1" diameter ball. On the special scale used, zero indentation is 200.

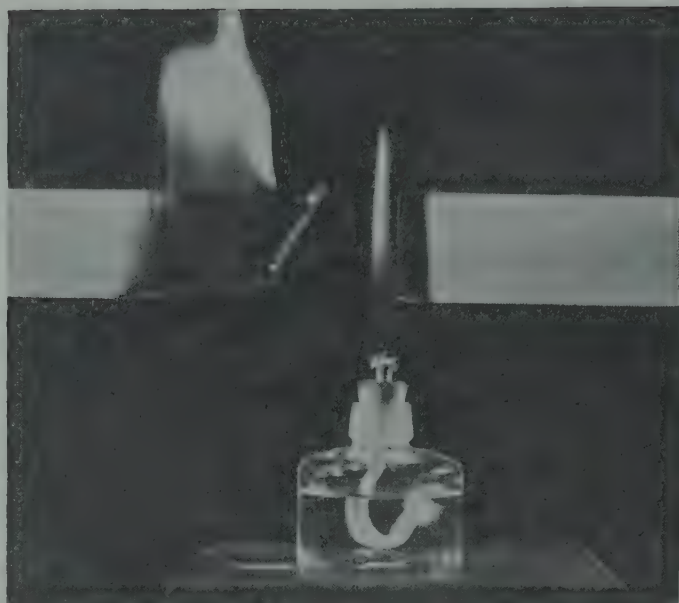


FIG. 24.13. Non-flammability and resistance to flame propagation of wood treated with methylolurea is shown by this test in which flame from alcohol lamp was placed at junction of untreated (left) and treated (right) pieces. (Courtesy Du Pont Company.)

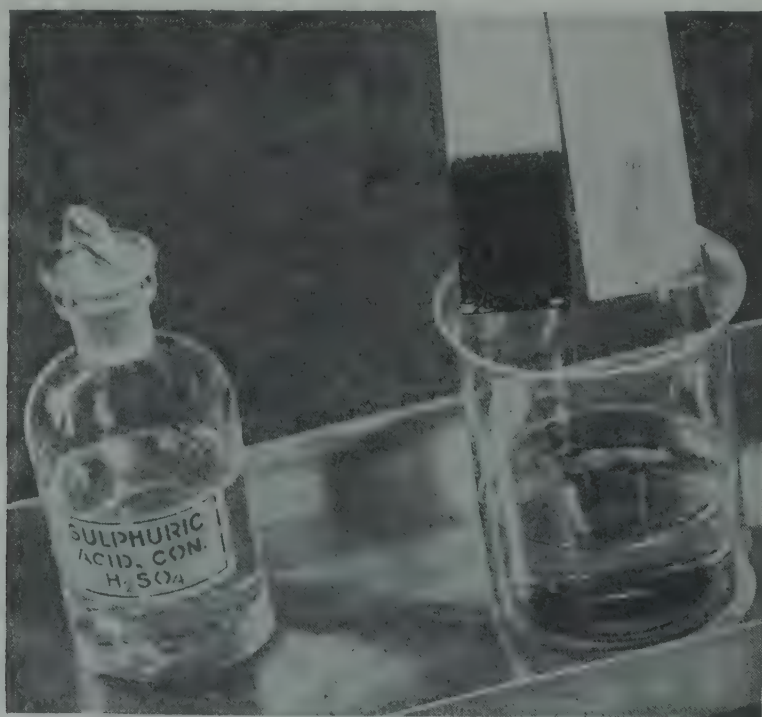


FIG. 24.14. Wood treated with methylolurea is rendered resistant to chemical attack as shown in test above in which untreated (left) and treated (right) piece were dipped simultaneously into sulphuric acid. (Courtesy Du Pont Company.)

half-inch section of steel plate. The resistance to burning and to the action of concentrated sulfuric acid are shown in Figures 24.13 and 24.14 respectively.

By adding a suitable dye to the impregnating solution of methylolurea, the wood is colored all the way through. Another interesting feature is that veneers, which have been impregnated and dried to a point where the resin formed is still fusible, can be used without any other adhesive to form plywood. With the application of heat and pressure, these treated veneers are self-bonding.

Review Questions

1. Describe the steps involved in a laminating operation.
2. What is the difference between rolled tubing and molded tubing?
3. List the valuable properties which are exhibited by a decorative laminate.
4. What differences of technique are involved in a comparison of high and low-pressure laminating?
5. Illustrate diagrammatically two methods of applying fluid pressure to a laminated structure during cure.
6. What are the advantages of heating by high frequency?
7. Describe the methods used for the impregnation of wood.

CHAPTER XXV

COATINGS

The practice of applying synthetic resins to fields of decorative or protective coatings is one which is largely based upon plasticization of the resin by the addition of solvents.

Three fundamental types of coatings may be listed, depending upon the method used to cause drying or hardening of the film. These three types are known as

1. Solvent-drying,
2. Air-drying,
3. Heat-hardening.

The first class includes those coatings which deposit a film of the resin as a result of the evaporation of the solvent. The second class of coatings involves the use of drying oils or modified resins which harden as a result of atmospheric oxidation and polymerization. The third class consists of those resins which can be polymerized and thus hardened by the application of heat. Although the above classification is of value in determining the type of resin to be used in a given application, it is not rigid, and there is a certain amount of overlapping. For example, in the use of a heat-hardening resin, a solvent may also be used and there will be some evaporation of the solvent (class 1) both prior to and during the application of heat (class 3).

In the coatings industry, the following classifications are made:

1. *Spirit varnishes*: Coatings compounded by dissolving a resin in a suitable solvent or mixture of solvents. The most common example of this type is shellac.

2. *Lacquers*: Coatings based upon a cellulose derivative as the main constituent. These may or may not contain a drying oil as a basic ingredient.

3. *Oil varnishes*: This group is prepared by the joint use of an oil and a resin. Accordingly, it is often referred to as an *oleoresinous varnish*. When a thermosetting resin is used, heat must be applied in order to cause curing or hardening of the resin. If a thermoplastic resin is used, the heat may be applied to accelerate the drying of the oil.

4. *Enamels*: Highly pigmented varnishes used to produce colored or opaque films comprise this category.

5. *Paints and calcimines*: Although this group is not involved in a discussion of synthetic resins or plastics the terms are described here for the purpose of clarity. A paint is composed of a pigment dispersed in an oil vehicle. Hardening occurs as a result of oxidation and polymerization of the oil film. Calcimines are fundamentally water paints for they consist of a colloidal binding agent such as casein or glue mixed with pigments in a water solution.

Varnishes.—The use of finishes applied from solutions or dispersions has long been practiced as a means of producing a decorative or protective film on the article being coated. The characteristics which are desired and tested in a coating application of a resinous base differ greatly from the performance which is sought in a molding or laminating application. This is particularly true because of the fact that the use of coatings is largely dependent upon the properties of a *thin* continuous film. Accordingly, properties of chemical resistance, abrasion, weathering, diffusion, adhesiveness, and colorability are of very great importance. In many cases, undesirable features which do not interfere with the use of molded objects are evident in this application. For example, a solid molded block of plastic may show excellent resistance to mineral oils, but the same material may fail as a protective coating because of a high rate of diffusion of such oils through the thin film used as a coating.

The history of the varnish industry, therefore, has been a continuous effort to produce favorable combinations of oils and resins. It has long been known that such oils as linseed or tung, when exposed to air, are capable of hardening as a result of oxidation and polymerization. The films thus obtained, however, lack hardness and gloss. Resins are added to impart those properties which were lacking. The relatively soft gums and resins (e.g., gum dammar), which were first used, have been replaced to some extent by the harder fossil resins such as copals.

The technique of preparing a varnish has evolved from the efforts to improve the natural resin being used. Because of the relative insolubility or incompatibility between the fossil resins and the oils, a cooking, or heat depolymerization, of the resin is required. This process, known as "*gum running*," consists of heating the resin slowly to temperatures of 310–340° C. in copper, stainless steel or aluminum kettles. The oil, which also may be pre-treated to aid its hardening, is added to the hot resin and the mixture is stirred to

form a homogeneous solution. When sufficiently cooled, a solvent or thinner, which is generally a petroleum fraction, is added, and the varnish is clarified by centrifugal sedimentation.

The oils used in this procedure are characterized by their drying properties, which result from the fact that they contain unsaturated linkages. The degree of unsaturation, as shown by values of iodine number, is often regulated by treatment of the oil preliminary to its use in a varnish. For example, the industry commonly refers to "boiled oils" and to "blown oils." The former term refers to those oils which have been subjected to a heat treatment in the absence of oxygen to effect partial bodying of the oil by polymerization through the olefinic linkages. "Blown oils" are formed by heating at a lower temperature and by blowing air through them. By both treatments, the unsaturation is reduced, partial hardening results, and final hardening of the film is hastened. When deposited as a film, the oil forms a soft coating after the volatile solvent has evaporated from the varnish. Although the exact nature of drying has not been proved, increase of molecular weight and decrease of iodine value point to a reaction caused by saturation of the olefinic linkages either by carbon-carbon polymerization or joining of neighboring chains through oxygen linkages. (See pp. 322-324.) The increase in molecular weight, in any event, results in hardened and inert films.

In the compounding of a varnish, also, an ingredient known as a drier is generally included. Materials of this type act as special catalysts for the drying reaction. The common ones now in use include the lead, manganese and cobalt salts of high molecular weight aliphatic acids, or naphthenic acids. These oil-soluble salts are used to the extent of 0.1%-0.2%, based on the weight of the oil. If, on the other hand, inhibitors of the drying reaction are desired, they may be chosen from the list of antioxidants commonly used in rubber.

The application of natural resins to coatings compounded from solvent and resin alone should also be noted. These varnishes are formed simply by dissolving certain resins, particularly shellac, in alcohol or other inexpensive solvents. Although one of the first varnishes to be used, shellac is still one of our outstanding *spirit varnishes*.

Major changes in the varnish industry have followed one another in rapid succession as synthetic resins appeared as replacements for natural products. The uniformity, and improved compatibilities, together with the possibility of "tailoring" of the molecule to produce specific properties, are the three major reasons for the rapid rise in

the popularity of varnishes made from synthetic resins. Regulation of solubility in the oils being used, incorporation of drying properties in the resins themselves, and ability to complete the polymerization reaction after deposition of the film are typical factors which are particularly advantageous. The most popular resins in this application include the phenol-formaldehydes of both the modified and unmodified types; alkyds of many different types including the unmodified, drying, and resin modified; urea-formaldehydes for use in baking enamels, particularly, when good color stability is necessary; and the resins obtained as a result of the diene synthesis from maleic anhydride with rosin or terpenes.

From such ingredients, the varnish may be compounded as with natural resins. Variation of the ratio between oil and resin changes the "oil length" from those in which oil is predominant (long oil), to those in which the oil is present in a smaller amount (short oil). To the combination of resin and oil, driers and diluting solvents may be added.

Lacquers.—The lacquer industry is founded upon the use of cellulose derivatives as the main film-forming ingredient of the coating. The availability and low cost of cellulose nitrate are responsible for the introduction of this type of material into the coating industry. The film strength and chemical inertness of cellulose nitrate have long been recognized, but the popularity of this material for solution application resulted as a consequence of improved or modified methods of manufacture. Originally, the high viscosity in solution, brittleness, poor weathering, and lack of adhesion were among the undesirable characteristics when films or finishes were attempted. The cellulose chain, however, may be degraded, with regulated control, by hydrolytic action either before or after esterification. By heating cellulose nitrate and water in a pressure kettle at 125° C., a hydrolytic cleavage of the cellulose chain is accomplished without any change in the nitrogen content. The resulting cellulose nitrate chains contain approximately 200 glucose units and are much more satisfactory for use in lacquers than esters containing longer chains. This degraded cellulose nitrate produces a solution having a lower viscosity, which deposits a film having increased adhesion and better flexibility than previous cellulose nitrate products.

As the art of compounding and the preparation of new synthetic types have developed, other cellulose derivatives have been applied. At the present time, formulation of lacquers may be accomplished with any of the cellulose esters or ethers. The compounding of a

lacquer varies according to the properties desired and the application technique being used. The more important components of a lacquer are:

- Cellulose derivative
- Modifying resin
- Plasticizer
- Oil
- Solvent (active and latent)
- Diluent
- Pigment or dye
- Stabilizer

The essential functions of each of these components will be discussed briefly. A more detailed consideration of the synthetic resin types and the cellulose derivatives will then be given.

Cellulose Derivative: This is the essential film-forming ingredient. The other components are important in so far as they modify the properties of the film and are essential for the proper forming or deposition of the film.

Resin: A synthetic resin such as an alkyd or phenolic, or a natural product such as gum dammar is used in conjunction with the cellulose derivative, in order that the adhesiveness, gloss, hardness, chemical resistance, and strength of the oleoresinous films may be retained. These materials are generally hard diluent resins which are readily soluble in the cellulose ester solvents and are compatible with the cellulose derivative in the film. Typical products include gum dammar, ester gum (glycerol-abietic acid reaction product formed by the use of rosin as the source of abietic acid), unmodified phenolics, and simple or oil-modified alkyds.

Plasticizer: The plasticizer in a lacquer is used for the same purpose and is subject to the same restrictions as a plasticizer in a molded product. Flexibility and strength of the film are dependent upon the amount and type used. The combination of nitrate cellulose nitrate and diluent resin is extremely brittle without the presence of a non-volatile plasticizer in the film. Such characteristics as adhesion, binding of the pigments, and impact resistance are also generally improved.

Oil: Loss of the plasticizer from the film by exposure over a long period of time is reduced by including either an oxidizable or non-drying oil in the formulation. If this ingredient is used with the cellulose derivatives without an accompanying chemical plasticizer, "bleeding-out" of the oil will occur because of the lack of sufficient

solvency. In the presence of a plasticizer which acts as a mutual solvent of both, however, the oil remains compatible with the cellulose product. By inclusion of the oil, increased flexibility, adhesion and toughness may be obtained. Also, the drying characteristics may be conveniently controlled if a slow-drying lacquer is desired. Typical oils which may be used include raw castor oil, blown soyabean and treated linseed oil.

Active Solvent: The true solvents of the cellulose esters—broadly esters, ketones, and monoethers of dihydroxy alcohols—are used as the active solvents of a lacquer. The drying time is regulated by the volatility of the solvent chosen. Lacquers which dry to a firm film as rapidly as 2–3 minutes or as slowly as 2–3 hours may be formulated by proper choice of solvent. Limiting conditions, however, are the undesirable “water blush” caused by condensation of moisture on the film if too rapid a drying time is attempted and the excess time required before polishing or sanding if too slow a drying schedule is used. The viscosity characteristics are also dependent upon the choice of active solvent as well as upon the less active solvents used with it.

Latent Solvents: Various organic solvents, such as alcohols, which do not normally exert a solvent effect upon the cellulose esters may act as latent solvents. (See p. 216.) These materials, when used in combination with active solvents, aid in producing a solubilizing effect and, at the same time, they produce an appreciable effect upon the viscosity of the lacquer.

Diluent: This portion of the solvent blend does not exert any true solubilizing effect upon the cellulose derivative. Instead, its functions are to extend the more costly solvents, thus decreasing the cost of the lacquer, and to decrease the viscosity of the solution.

The blending of solvents and diluents for use in lacquers is perhaps the most intricate and specialized phase of the compounding. A decision must first be reached as to whether a quick, medium or slow drying lacquer is most suitable for a specific application. Then, appropriate solvents for the cellulose derivative and the modifying ingredients must be selected. Typical solvent blends for quick and slow drying lacquers are given in Table I-25.

When considering the compatibility of the cellulose derivative and modifying resin, it must be remembered that the true solvents of the cellulose materials are often non-solvents for the modifying resins. Esters and ketones are the most popular solvents for cellulose derivatives, while alcohols or hydrocarbons are most suitable for the modifying resins. Thus, it is inevitable that the two factors, adjust-

TABLE I-25^a

Quick-drying	Per Cent (Vol.)	Medium-drying	Per Cent (Vol.)	Slow-drying	Per Cent (Vol.)
Methyl ethyl ketone	10	Butyl acetate	30	Butyl propionate	20
Isopropyl acetate	5	Butyl alcohol	10	Butyl alcohol	15
Ethyl alcohol	15	Toluene	60	Amyl alcohol	10
Isobutyl acetate	15			Xylene	30
Secondary amyl acetate	5			Petroleum naphtha (240–290° F. range)	20
Toluene	50			Ethyl lactate	5
	100		100		100

^a Simonds and Ellis, *Handbook of Plastics*, p. 449, D. Van Nostrand Co., New York (1943).

ment of drying speed and regulation of compatibilities, should result in complex solvent blends. One of the major problems in the formulation of lacquers is that of maintaining complete homogeneity during the drying process. If an excess amount of the true cellulose solvents remains in the film as it dries, the "gum" or modifying resin will separate prematurely in the film and cause an effect known as "gum blush." If, on the other hand, an excess amount of the gum solvent is present at any time during drying, the cellulose derivate separates and this results in "cotton blush." The proper balance must be maintained by a relatively constant ratio of the solvent and diluent portions of the solvent blend during drying. Temporary changes in the proper ratio may result in blushing of either the gum or cotton but if the ratio is corrected as drying continues, the opalescence due to blushing may disappear and a satisfactory film may be formed.

Pigments and Dyes: The coloring agents of a lacquer may consist of either inert inorganic materials or organic dyes. In the case of solvent-soluble dyes no difficulties of mixing are experienced. The insoluble dyes and pigments, however, may be mixed with the lacquer only after a preliminary dispersing by ball-milling of the powder in one of the solvents to be used. By means of such equipment as the ball-mill, pebble-mill, or steel-roll grinder, the particles of pigment may be broken up and maintained in dispersed form by the protective action of a suitable dispersing agent.

Stabilizer: A stabilizer such as phenyl β -naphthylamine is often included in a lacquer formulation to prevent decomposition with

aging of the cellulose derivative. This is particularly true of cellulose nitrate types.

RESIN TYPES USED IN COATINGS

Most of the basic resins described in Section II may be applied as coating compounds. Their fundamental characteristics, of importance to coating applications, will be summarized here.

Phenolics.—This type of resin is used for the most part in varnishes where quick-drying properties, durability, weather resistance, gloss, and hardness are desired. Four-hour drying types of varnishes, baking enamels, spar varnishes and quick-drying primers are prominent in this class. In the compounding of a varnish, the unsubstituted phenol-formaldehyde polymers do not readily mix with either drying or non-drying oils. More soluble products can be obtained either by modification of the phenolic resin with natural resins—particularly abietic acid (rosin) or copals—or by using a para substituted phenol in the original condensation polymerization with formaldehyde. In the first instance, a low-cost oil-soluble resin is obtained by heating the rosin with the phenol-formaldehyde polymer prior to mixing with the oil, or by adding the natural resin directly to the mixture of phenol and formaldehyde at the beginning of the polymerization reaction. By the use of rosin a soft product may be produced, while a hard product is formed when copal is substituted for the rosin. The condensation polymers obtained when para substituted phenols such as *t*-butyl, *t*-amyl, octyl and phenyl phenols are allowed to react with formaldehyde exhibit oil solubility. Some degree of oil solubility is also obtained in the cresol or xylenol mixtures with phenol when allowed to react partially with formaldehyde. These oil-soluble polymers form films which are characterized by alkali resistance, color retention, durability and hardness.

Resins of the phenolic class are also used in lacquer formulations to improve the rubbing characteristics, film strength, and adhesiveness.

Alkyds.—This class of resins is basically the most important in the varnish industry. A review of the properties and the variations of this type as discussed in Chapter XVI is recommended in connection with this study. The principal types of alkyds used in the coating industry will be discussed briefly.

Unmodified: This class consists mainly of the glycerol-phthalic acid reaction products. Poor compatibilities with other resins, both natural and synthetic, limit their use in the manufacture of varnishes, but favorable electrical properties result in some application as cable

coatings. Addition to cellulose acetate or cellulose nitrate lacquers is recommended for special properties of hardness, durability, and adhesion.

Modification by Fatty Acids: Addition of a saturated fatty acid or the oil from which it may be obtained by hydrolysis, results in the formation of a relatively tough, elastic, flexible, product. Such acids as oleic, stearic and palmitic or oils such as castor oil and cocoanut oil are commonly used. The resultant products are not valuable in the manufacture of varnish, but compatibility with cellulose derivatives makes them valuable in lacquer formulations. Their films are toughened by small amounts of cellulose nitrate and such a combination produces lacquers noted for color retention, durability, weathering resistance and toughness. Many of the beneficial properties stem from the fact that a high ratio of resin to cellulose nitrate may be used. Such lacquers are used in the automotive, linoleum, leather, and metal industries.

Modified with Unsaturated Acids or Oils: This group comprises the most popular class of alkyds for use in air-drying or baking types of coatings. Such base alkyds as glycerol-phthalates or maleates may be allowed to react directly with a drying oil such as linseed, soya, or dehydrated castor or the acids formed from these oils may be used. The properties obtained depend upon the ratio of oil to resin used, i.e., oil length. In general, however, properties of adhesion, toughness, color retention, durability when properly cured, and low cost are associated with the varnishes in which these are used.

Resin Modified: The natural-resin modified alkyds are typified by the reaction products of rosin with the alkyd polyester. Hard, brittle resins of low strength and poor flexibility result from this combination, but the resins of this class are often used in lacquer formulations, because of their compatibility with cellulose nitrate. They are particularly useful for interior applications where quick drying schedules are desired. When the rosin-glycerol-phthalic acid combination is combined with a drying oil, some increase in flexibility results but appreciable hardness is retained. Interior varnishes with good properties of gloss, hardness, and low cost result. The modification is not limited to rosin but may be extended to copals, dammar, shellac, or terpenes.

Alkyds may also be modified by the use of a synthetic resin such as a phenol-formaldehyde or urea-formaldehyde condensate. The synthetic resin imparts hardness and gloss to the alkyd and the latter in turn, increases the flexibility of the former. The combination results in air-drying or heat-baking finishes which are useful in a

wide field of applications. Increased water resistance, chemical resistance, and hardness generally result.

Ureas and Melamines.—The advantage of these amino-aldehyde resins in the coating industry is particularly evident in their use in baking types of coatings where colorability is a prime factor. Both types of amino condensates are used in the form of solutions in alcohols and hydrocarbons. Their principal application is in conjunction with resins of the alkyd class. Most types of alkyds are readily compounded with ureas and melamines, although in some cases the degree of polymerization of the amino resin may have to be regulated before obtaining complete homogeneity. The combination of amino and alkyd resins results in many properties not possessed by either alone. Baking schedules are speeded, hardness and toughness are combined in the same film, weathering resistance is increased, resistance to water vapor is improved, and better adhesion results in some cases.

The melamines, in general, are superior to the ureas in retention of color and luster at high temperatures, heat resistance and, therefore, increased hardness at elevated temperatures, and greater stability to long baking schedules (see Figures 11.5 and 11.6, pp. 206, 207). The ureas, on the other hand, are superior in chemical resistance, durability, flexibility of the film, adhesion to a variety of surfaces, and long service under exposed conditions. Typical coating applications of the amino resins include automotive, refrigerator, bathroom, stove, heater, and truck-body enamels.

CELLULOSE DERIVATIVES USED IN COATINGS

Cellulose Nitrate.—In previous discussions of cellulose nitrate, the use of this plastic in synthetic coatings has been emphasized. A cellulose nitrate of nitrogen content in the range of 11.5–12% is generally chosen. Since the application is one requiring ease of solution, the molecular weight of the cellulose nitrate is lowered by cleavage of the cellulose chain. From this base ingredient, coatings which are widely diversified in their recommended methods of application and drying may be produced. The final characteristics of a particular coating will depend upon the compounding ingredients selected for use with the cellulose derivative. The functions of these compounding agents were discussed earlier in this chapter. Three examples of cellulose nitrate lacquer formulations are listed in Table II-25.

TABLE II-25

Clear Bronzing Lacquer ^a	Per Cent by Weight	Clear Gloss ^a Rubbing Lacquer (Non-volatile 21%)	Per Cent by Weight	Gloss Brass Polishing Lacquer ^b	Per Cent by Weight
30-40 ° sec. nitrocellulose (dry basis)	16	½ sec.° nitrocellulose (dry basis)	9	15-20 sec.° nitrocellulose (dry basis)	8
Elemi gum	3	Modified alkyd (non-drying acid type)	2	Maleic modified alkyd	6.5
Ester gum	3	Resin modified phenolic	7	Dibutyl phthalate	3.5
Castor oil	4	Tricresyl phosphate	2	Ethyl acetate	20
Ethyl acetate	10	Castor oil	1	Butyl acetate	12
Butyl acetate	20	Ethyl acetate	10	Butyl alcohol	12
Toluol	26	Butyl acetate	15	Toluol	38
Ethyl alcohol	10	Butyl alcohol	6		
Butyl alcohol	8	Amyl alcohol	3		
		Toluol	25		
		Xylol	15		
		Ethylene glycol monobutyl ether	5		

^a Simonds and Ellis, *Handbook of Plastics*, p. 450, D. Van Nostrand Co., New York.

^b *Ibid.*, p. 451.

^c The designation of nitrocellulose in terms of seconds is a measure of the viscosity of a standard solution of the sample of nitrocellulose. The number of seconds is the time required for a steel ball, 0.3120-0.3130 inch in diameter and weighing 2.035 g. \pm 0.010 g., to fall vertically through ten inches of a standard solution of the nitrocellulose. The standard solution generally contains 12.2% of nitrocellulose (dried to constant weight at 50° C.) dissolved in a mixture of ethyl acetate, denatured alcohol and toluol, though more concentrated solutions are used when low viscosities (< 6 seconds) are encountered.

Compounding of the cellulose nitrate for a particular coating application depends primarily upon the method of application, the speed of drying desired, the surface finish being coated, and the specific properties desired in the film. The first variation is that of the cellulose nitrate itself. If a low viscosity lacquer with a fairly high solids content is desired, a $\frac{1}{4}$ - $\frac{1}{2}$ second cellulose nitrate is used. This type of lacquer is required for application to a porous surface. For the application of a thin film to a non-porous surface, a high viscosity lacquer, such as that made from 1000 second cellulose nitrate, is necessary. The modifying resins may be chosen from a long list of natural or synthetic types. Characteristics of hardness, sanding, toughness, adhesion, speed of drying, chemical resistance, and color stability are regulated by adjustment of the modifying resins. The most suitable solvents for cellulose nitrate are esters,

ketones, mixtures of esters and alcohols and monoalkyl ethers of polyhydroxy alcohols.

Remaining Cellulose Esters.—The acetyl and mixed esters of cellulose are also applied in many cases in lacquers as replacements for cellulose nitrate. Cellulose acetate is the most common of these, but in spite of the fact that improved flame resistance has favored the use of this derivative, its popularity in the coating industry has been limited. Such favorable properties as resilience, light and heat stability, toughness, and low flammability are offset by such undesirable characteristics as low solubility, decreased adhesion, and poor water resistance. Some growth in recent years, however, has resulted from the adaptability of acetate lacquers to interior finishes of aircraft and automobiles where the safety factor of decreased flammability is of such great importance. The lower solubilities of the cellulose acetates necessitates a careful selection of solvents. Esters and ketones are the most popular true solvents. In either case, however, some alcohol is generally added to improve the solubility and lower the viscosity. Lacquers of low solids content are often encountered because of the difficulty of producing a low viscosity. The water resistance of acetate films is low. This fact limits the consumption for outdoor purposes. There is some tendency toward wrinkling and whitening of the film if the acetate is exposed to weathering for long periods.

The properties of the acetate lacquers may be modified to a limited extent by compounding with diluent resins, plasticizers, or oils. Just as the solubility of cellulose acetate is lower than that of cellulose nitrate, so, too, the acetate exhibits decreased compatibility with modifying agents. Straight phenolics, some types of alkyds, (particularly those modified with saturated acids), and polymethylmethacrylate may be used in conjunction with the acetate. This allows formulation for either a solvent-evaporating or a heat-hardenable type of coating.

The mixed esters—particularly cellulose acetate-butyrate and cellulose acetate-propionate—are also used as lacquer bases. These derivatives have certain advantages over cellulose acetate. Improved solubility, compatibility, water resistance, and chemical resistance of these types has caused replacement of the acetate in many applications. In addition, the properties of excellent light-fastness and weather resistance may be mentioned. The propionate mixed ester is used more frequently than the mixed acetate-butyrate, because of superior miscibility. By compounding with such synthetics as straight phenolics or modified alkyds and such natural

resins as dammar, gum elemi, and rosin derivatives, the adhesion and toughness of the film are improved. The usual plasticizers for cellulose derivatives are applicable.

Ethyl Cellulose.—The chief type of cellulose ether which can be incorporated into a lacquer is ethyl cellulose. A review of the properties of ethyl cellulose (Chapter XII) will emphasize the reasons why this derivative is so popular in the coating industry. First, the solubility of ethyl cellulose in a solvent blend containing a high proportion of aromatic solvent, permits manufacture of a satisfactory lacquer at a relatively low cost. Extreme ranges of compatibilities with modifying resins, oils and waxes permits wide variations of compounding formulas. This cellulose derivative, for example, may be incorporated into varnishes to improve the toughness and hardening quality of the film. It may be mixed with waxes to produce paper coatings, and with diluent modifying resins—particularly those of the alkyd class—to form flexible, tough, water-resistant, and strongly adhesive coatings which have become popular in aircraft, automotive, electrical, and marine applications. Resistance to low temperatures, heat, light, greases and oils, and its high dielectric properties are particularly valuable.

The field of synthetic coatings is thus based upon the use and compounding of several types of base resins. The most important of these have been listed, but many others are being used for specialized applications. The vinyls, acrylates, and polystyrenes are popular thermoplastics, which are used as coatings. Esterified natural resins such as ester gum or esterified copal are valuable because of their improved compatibility with cellulose derivatives. Miscellaneous types such as terpenes or rubber derivatives possess properties which are often of value for specific applications.

Review Questions

1. Indicate the composition of each of the following types of coatings:

spirit varnish
lacquer
oleoresinous varnish.

2. What is meant by the terms:

“gum-running”
“blown oils”
“bleeding-out”
latent solvent?

3. Describe the method of preparing of an oleoresinous varnish.
4. Outline a typical lacquer formulation and state the reasons for the use of each of the ingredients.
5. Why are para substituted phenolic resins so popular in the coatings industry?
6. What are the principal properties obtained by the use of each of the following resins in coatings:

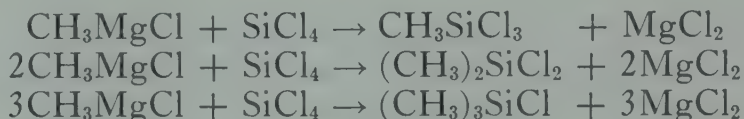
cellulose nitrate
alkyds
ureas and melamines?

APPENDIX I

SILICONE RESINS

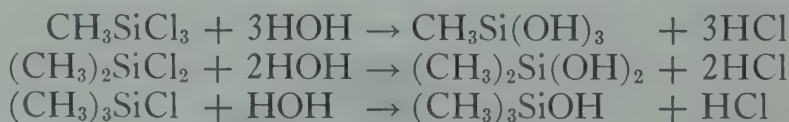
A very recent development in the field of synthetic resins is the utilization of polymeric silicones. These polymers are formed as a result of the condensation polymerization of silanols, and can be obtained as mobile, volatile liquids soluble in most organic solvents or as infusible, insoluble solids.

The formation of this interesting class of polymers can be illustrated by describing the preparation of polymeric methyl silicones. The first step in their preparation¹ is the interaction of silicon tetrachloride² with methylmagnesium chloride to form methylsilicon chlorides. As shown by the following equations, three methylsilicon chlorides are possible:



By varying the ratio of Grignard reagent to silicon tetrachloride, it is possible to obtain chiefly the mono-, di- or tri-methyl silicon chloride, but it is probable that the reaction product always contains varying amounts of the other two. The reaction can be carried out by adding slowly an absolute ether solution of the Grignard reagent to an absolute ether solution of silicon tetrachloride at or below room temperature.

The reaction mixture is then poured onto cracked ice, which causes the hydrolysis of the methylsilicon chlorides, forming silanols



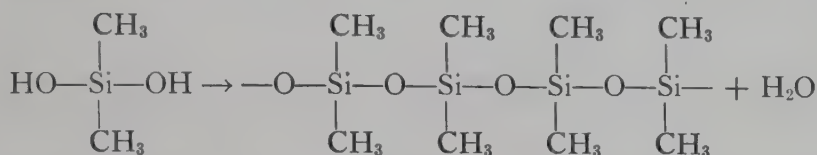
These silanols are not usually isolated, because they condense with each other immediately with the loss of water, forming products which are soluble in ether. The ether solution is washed free of

¹ Rochow, U. S. Patent 2,258,218 (1941).

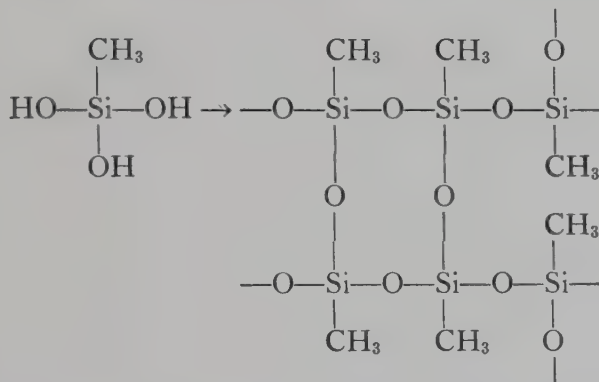
² Tetraethyl orthosilicate may be used in place of silicon tetrachloride.

acid and the ether evaporated, leaving a viscous liquid which is suitable for use in adhesives and surface coatings, and which can be polymerized further when heated.

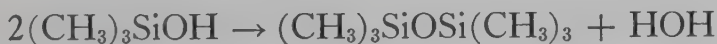
The name "silicone" was previously ³ used by Kipping to describe compounds of the type R_2SiO . Since this is the unit found in polymers formed from a dialkyl silanediol ($R_2Si(OH)_2$), these polymers are called polymeric silicones or, frequently, just silicones. From examination of the formula for dimethyl silanediol, it is obvious that a linear condensation polymer can be formed by the loss of water.



Methyl silanetriol, containing three reactive groups in each molecule, is capable of forming a cross-linked structure, e.g.,



Since trimethyl silanol has only one hydroxyl group, two molecules can react to form a silicon ether or disiloxane.



If trimethyl silanol is present in a mixture of mono- and di-silanol, it can function only to terminate the polymerization reaction. For many purposes, a mixture of mono- and di-silanol is desirable in order to provide cross-linking which is so important in rendering resin compositions insoluble and infusible.

The polymer formed by the interaction of 1.75 moles of methylmagnesium bromide and one mole of silicon tetrachloride, when heated gradually to 200° C. over a period of 24 hours and then kept

³ Kipping, *J. Chem. Soc.* **91**, 218 (1907).

at 200° C. for 48 hours, is a clear colorless, odorless, horny solid. An analysis indicated that it contains 1.41 methyl groups for each silicon atom. It has a dielectric constant of 3.7 at 26° C., and power factor, at 60 cycles, of 0.008 at 26° C. It can be heated at 200° C. in air for several days without melting, though it does become more brittle. However, at 300° C. in air it oxidizes and disintegrates in 24 hours, although it can be heated in a vacuum for 24 hours at 550° C. without disintegration. In this case, water is gradually eliminated as the temperature rises above 200° C.

Methyl silicones containing 1–1.5 methyl groups for each silicon atom can be used as bonding agents in the formation of laminated mica products. These products are characterized by high dielectric strength and the ability to withstand temperatures as high as 250–300° C. Bentonite sheets treated with methyl silicones are suitable for high temperature insulating applications. A partially polymerized silicone dissolved in a volatile solvent can be spread onto a wire which is then heated to volatilize the solvent and to produce further polymerization. The resulting coating is an excellent insulator.

Silicones other than the methyl silicones are finding interesting applications. For example, highly chlorinated (at least three chlorine atoms for each aromatic ring) diaryl silicones have been found to impart flame resisting properties when applied to inflammable materials such as cotton, silk, wool and wood.

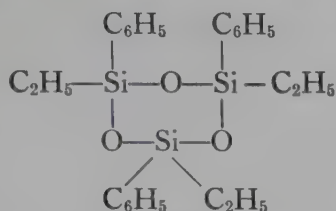
Liquid silicones have been synthesized which have a very low rate of viscosity change over a wide range of temperatures (high viscosity index), have higher flash points than petroleum oils of equivalent viscosity, are chemically inert and non-corrosive to metals and are highly resistant to oxygen and oxidizing agents.

Silicone rubbers have been developed which can be used at temperatures of 200° C. for a period of several months without hardening or losing their resiliency. On the other hand, at the low temperature of – 65° F. (– 48° C.), silicone rubbers retain most of their resiliency. The brittle point is reached at – 80° F. (– 62° C.). Silicones containing alkyl groups exhibit more rubber-like characteristics than those containing aryl groups.

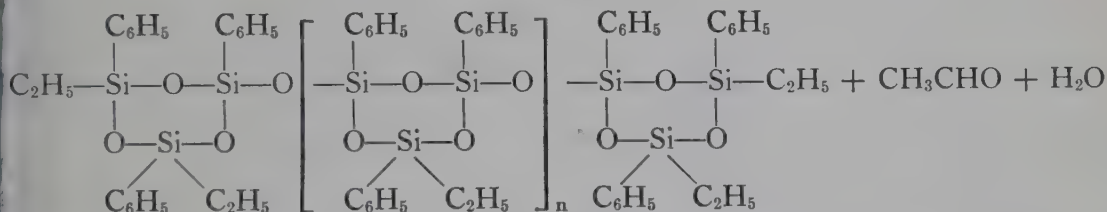
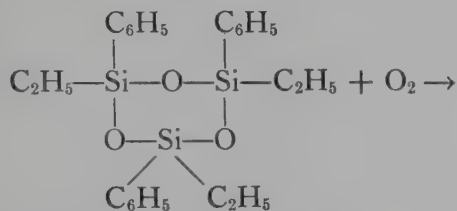
Additional data concerning the structure of polymeric silicones have been described by Hyde.⁴ Evidence that the polymeric silicones first formed exist as cyclic trimers is found in the fact that the product isolated by the hydrolysis of phenylethylsilicon dichloride

⁴ Hyde, Brit. Pat. 561,136 (1944).

has a silicon content and a molecular weight which agree very closely with the theoretical values for the following formula.



When this trimer is further polymerized by heating to 200–300° C. at the same time that air is bubbled through it, acetaldehyde is evolved, indicating that ethyl radicals are being oxidized. The viscosity of the liquid also increases, indicating that further polymerization is occurring.



When polymerization has proceeded to the sticky, viscous stage in which the polymer is still soluble in toluene, molecular weight determinations indicate that $n = 2$ in the above formula. Further heating produces a polymer which is insoluble in toluene. This process is believed to be accompanied by the formation of cross-linkages between linear chains. These cross-linkages are also believed to be Si—O—Si linkages formed as a result of the oxidation of ethyl groups.

When the trimeric phenyl ethyl silicone is heated to 170–180° C. and a dilute aqueous solution of hydrochloric acid containing a trace of ferric chloride is added to the polymer, hydrolysis occurs with the liberation of benzene and the formation of a polymer having a formula similar to that given above, but with the phenyl and ethyl groups interchanged. This polymer is also soluble in toluene. However, further heating at higher temperatures, preferably with ferric chloride present, changes it to an insoluble, infusible polymer, probably as a result of the formation of cross-linkages. This type of polymer has

been particularly valuable for the impregnation of glass cloth for use as electrical insulation.

An interesting application of methylsilicon trichloride and dimethylsilicon dichloride is their ability to render various surfaces water-repelling. If the inside of a glass tube is exposed to the vapor of a mixture of the di- and tri-chlorides, and is then exposed to ammonia, a film is formed which prevents the wetting of the glass by water. Hence, no meniscus forms. A piece of previously dried cotton cloth was similarly treated and was so water-repellent that it could be made into a bag that would hold water. Scrubbing the bag with alcohol, acetone or soap did not destroy the water-repelling characteristics. Such treatment will obviously be of value in making such articles as shower curtains, awnings, umbrellas and raincoats.

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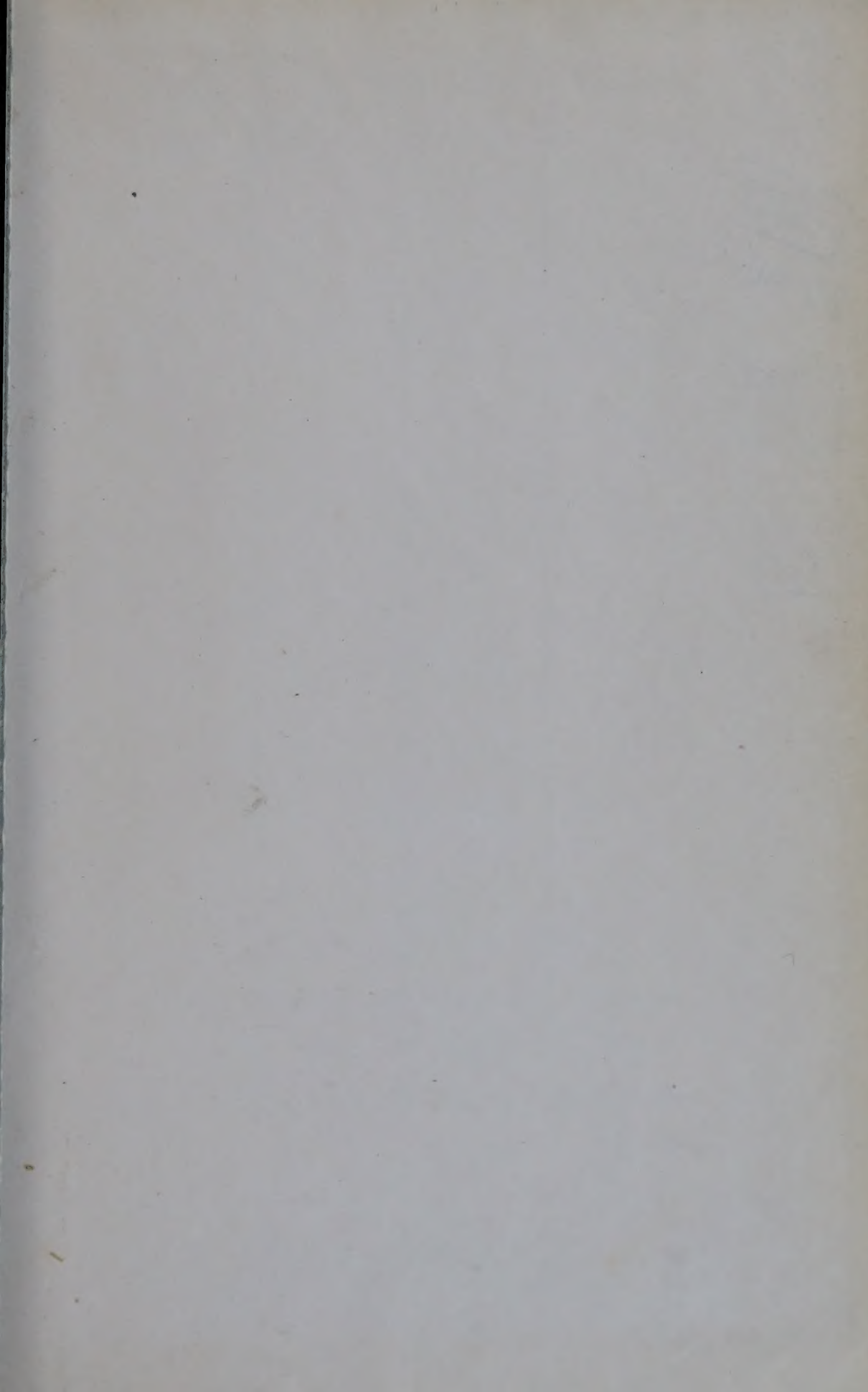
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